$$\times \int_{(R-1)\sqrt{\tau}}^{\infty} e^{-S^2}\left[1 - \tau\left(\frac{y^2 - (R-1)^2}{-(R-1)S + y[\tau y^2 + S^2 - \tau(R-1)^2]^{1/2}}\right)^2\right]^{1/2} dS \Bigg\}, \quad \text{for } 0 < y < R - 1 \tag{5a}$$

$$F^{(0)}(y,y;\beta) = \frac{1}{8(\pi D\beta)^{3/2}}(1 - e^{-\tau y^2}) + \frac{\beta\epsilon}{8\pi^2(D\beta)^{3/2}}\left(\frac{1}{2}\sqrt{\pi}\,(e^{-\tau(y-R+1)^2} - e^{-\tau(y+R-1)^2}) + \pi(R-1)\sqrt{\tau} + \tfrac{1}{2}\pi\sqrt{\tau}\right.$$

$$\times\{(y-R+1)\,\text{erf}\,[(y-R+1)\sqrt{\tau}\,] - (y+R-1)\,\text{erf}\,[(y+R-1)\sqrt{\tau}\,]\} + e^{-\tau y^2}$$

$$\times\Bigg\{\int_{(R-1)\sqrt{\tau}}^{\infty} e^{-S^2}\left[1 - \tau\left(\frac{y^2 - (R-1)^2}{-(R-1)S + y[\tau y^2 + S^2 - \tau(R-1)^2]^{1/2}}\right)^2\right]^{1/2} dS$$

$$-\int_{-(R-1)\sqrt{\tau}}^{\infty} e^{-S^2}\left[1 - \tau\left(\frac{y^2 - (R-1)^2}{(R-1)S + y[\tau y^2 + S^2 - \tau(R-1)^2]^{1/2}}\right)^2\right]^{1/2} dS\Bigg\}\Bigg), \quad \text{for } y > R - 1 \tag{5b}$$

where $\tau = 2\pi(\sigma/\lambda)^2$, $y = x_0/\sigma$, and erf is the error function.

The integrals in Eqs. (5a) and (5b) are negligible in a high-temperature approximation and can be omitted from the remainder of the calculation.

Substituting Eqs. (5a) and (5b) into Eq. (1) and using the high-temperature approximation that retains first-order terms in $\beta\epsilon$ and the first-order quantum correction λ/σ, yields

$$B_D(T) = \tfrac{2}{3}\pi\sigma^3\left[1 - \beta\epsilon(R^3 - 1) + (3/2\sqrt{2})(1 + \beta\epsilon)\lambda/\sigma\right]. \tag{6}$$

Equation (6) agrees with Nilsen's result to first-order terms in $\beta\epsilon$, which is a high-temperature approximation.

It should be noted that Eq. (6) does not reduce to the hard-sphere result for $\epsilon \neq 0$ in the limit $R \to 1$. This is a result of the high-temperature approximation used to calculate Eq. (6) from Eqs. (1) and (5). In the calculation of Eq. (6) the quantity $\text{erf}\,[(R-1)\sqrt{\tau}\,]$ was approximated by unity. This assumes $R \neq 1$.

I wish to thank Dr. Sigurd Larsen of Temple University for bringing Nilsen's work to my attention.

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Comments on the Alleged Validity of R_4 Invariance as a Symmetry for Electron Correlations*

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Recent indications that R_4 is a fairly good symmetry for two-electron atoms are shown to be unjustified.

Three recent papers[1,2] have indicated that two-electron eigenstates of the full Hamiltonian, including the $1/r_{12}$ interaction, are closely approximated by those linear combinations of configurations that form irreducible representations of the symmetry group of real rotations in four-dimensional space.

This group R_4 is well known to be responsible for the l degeneracy of the nonrelativistic hydrogen atom. Since it was not clear why it should be relevant to two-electron interactions, we undertook an investigation to see what physical basis could be attributed to the results of these authors. We have, however, been forced to the conclusion that there is no reason to believe that invariance under R_4 is even an approximate symmetry for the two-electron problem. Furthermore, we uncovered some sign reversals in the coefficients of the states described in Refs. 1 and 2, which when corrected negate the very results that prompted our investigation.

We consider two electrons in the $n = 2$ shell. Our attention was primarily focused on this shell because, even as a mathematical symmetry, it is precisely here that R_4 should best apply. For higher n there are arguments[3] to show that the associated group is really $R_{\sum_{all\ l}(2l+1)}$, i.e., R_{n^2}.

Adopting LS coupling, in the $n = 2$ shell there are two ^1S states and one each of $^1P^o$, ^3P, $^3P^o$, and ^1D. Since the only multiplicity is in the ^1S configuration, these are the only ones of interest for our study. The R_4 states are

$$(00)S: \tfrac{1}{2}|2s^2\,^1S\rangle + \tfrac{1}{2}\sqrt{3}|2p^2\,^1S\rangle ,$$

$$(20)S: \tfrac{1}{2}\sqrt{3}|2s^2\,^1S\rangle - \tfrac{1}{2}|2p^2\,^1S\rangle .$$

Comparing with the first two ^1S resonances of the doubly excited states of He as given by configuration interaction calculations[4] makes it immediately clear that though the numerical ratios are approximately correct, the phases are wrong. References 1 and 2 had incorrect signs in the coefficients of these states and hence came to the opposite conclusion.

This can also be seen by computing matrix elements of $1/r_{12}$ between these states using hydrogenic orbitals as in Ref. 2. The results are (in a. u.)

$$
\begin{array}{c c c}
 & (00)S & (20)S \\
(00)S & 0.1563 & -0.0541 \\
(20)S & -0.0541 & 0.2109
\end{array}
$$

whereas

$$
\begin{array}{c c c}
 & |2s^2\,^1S\rangle & |2p^2\,^1S\rangle \\
|2s^2\,^1S\rangle & 0.1504 & -0.0508 \\
|2p^2\,^1S\rangle & -0.0508 & 0.2168
\end{array}
$$

Thus, there is no improvement in going from the ordinary configuration basis to the R_4 basis.

We have computed all the $1/r_{12}$ matrix elements in the $n = 3$ and $n = 4$ shells and again come to the conclusion that the matrix of $1/r_{12}$ is not even approximately diagonalized in the R_4 basis. In some cases, for high n and high L, the off-diagonal ele-

ments in the R_4 basis are slightly smaller than in the configuration basis, but no systematic behavior was found. With the signs given in Ref. 2, and even then only for the ^1S states, the matrix is almost completely diagonalized. This fact that there is a basis set derived from the R_4 set with some sign reversals, which diagonalizes the configuration interaction, remains as a curious result for which we have no explanation.

We come next to the question of the reduction in the number of independent two-electron integrals. Consider again in Table I the $n = 2$ shell. The $\overleftrightarrow{W}$ are tensor operators defined by Feneuille.[5] Note that

$$\overleftrightarrow{W}^{(0K)}(l_a, l_b) = 2^{-1/2}\,\overleftrightarrow{V}^{(K)}(l_a, l_b) ,$$

where the $\overleftrightarrow{V}$ are defined by Judd.[6]

To get the R_4 tensors corresponding to $1/r_{12}$, one has to find all possible R_4 states with $L = 0$ arising from the product $[(00) + (20)]^2$. From Table II, there are three classes of such states: (00), (20), and (40). However, there are two kinds of tensors in each of the first two of these, so the actual number of irreducible tensors is five, which is the same as the number of Slater integrals, instead of three as stated in Ref. 2. An exactly similar situation arises in $(s+d)^N$ configurations.[5] There, in terms of R_6 and R_5, there are only five classes, but the actual number of relevant tensors is seven which is the number of Slater integrals in that problem.

Consequently, we must conclude that there are no linear relations between the Slater integrals, the number of independent two-electron integrals required remaining the same in the alternative basis.

A complete analysis of the Coulomb Hamiltonian is

$$
\begin{aligned}
H = \sum_{i>j} \{ &2F_0(ss)\overleftrightarrow{W}_i^{(00)}(s,s)\cdot\overleftrightarrow{W}_j^{(00)}(s,s) \\
&+ 6F_0(pp)\overleftrightarrow{W}_i^{(00)}(p,p)\cdot\overleftrightarrow{W}_j^{(00)}(p,p) + 12F_2(pp) \\
&\times \overleftrightarrow{W}_i^{(02)}(p,p)\cdot\overleftrightarrow{W}_j^{(02)}(p,p) + 2\sqrt{3}F_0(sp)
\end{aligned}
$$

TABLE I. Table of R_4 states and tensors.

	R_4 states	R_4 tensors
$(00)S$	$\tfrac{1}{2}|2s^2\,^1S\rangle$ $+\tfrac{1}{2}\sqrt{3}|2p^2\,^1S\rangle$	$\tfrac{1}{2}[\overleftrightarrow{W}^{(00)}(s,s)$ $+\sqrt{3}\overleftrightarrow{W}^{(00)}(p,p)]$
$(20)S$	$\tfrac{1}{2}\sqrt{3}|2s^2\,^1S\rangle$ $-\tfrac{1}{2}|2p^2\,^1S\rangle$	$\tfrac{1}{2}[\sqrt{3}\,\overleftrightarrow{W}^{(00)}(s,s)$ $-\overleftrightarrow{W}^{(00)}(p,p)]$
P	$2^{-1/2}(|2sp\rangle + |2ps\rangle\,^1P)$	$2^{-1/2}[\overleftrightarrow{W}^{(01)}(p,s) - \overleftrightarrow{W}^{(01)}(s,p)]$
D	$|2p^2\,^1D\rangle$	$\overleftrightarrow{W}^{(02)}(p,p)$
$(11)P$	$|p^2\,^3P\rangle$	$\overleftrightarrow{W}^{(11)}(p,p)$
P	$2^{-1/2}(|2sp\rangle - |2ps\rangle\,^3P)$	$2^{-1/2}[\overleftrightarrow{W}^{(11)}(s,p) - \overleftrightarrow{W}^{(11)}(p,s)]$

TABLE II. R_4 representations.

R_4 state	R_3 content	Dimension	
(00)	S	1	
(10)	SP	4	$(00) \times (00) = (00)$
(11)	PP	6	$(00) \times (20) = (20)$
(20)	SPD	9	$(20) \times (20) = (00) + (20)$
(22)	DD	10	$+ (22) + (31) + (11) + (40)$
(31)	$PPDDFF$	30	
(40)	$SPDFG$	25	

$$\times [\overleftrightarrow{W}_i^{(00)}(s,s) \cdot \overleftrightarrow{W}_j^{(00)}(p,p) + \overleftrightarrow{W}_i^{(00)}(p,p) \cdot \overleftrightarrow{W}_j^{(00)}(s,s)]$$

$$+ 2G_1(sp)[\overleftrightarrow{W}_i^{(01)}(s,p) - \overleftrightarrow{W}_i^{(01)}(p,s)]$$

$$\cdot [\overleftrightarrow{W}_j^{(01)}(s,p) - \overleftrightarrow{W}_j^{(01)}(p,s)]\} \quad .$$

We define the following:

$$\epsilon_0 = \tfrac{1}{2} \sum_{i>j} \overleftrightarrow{W}_i^{(00)}(s,s) \cdot \overleftrightarrow{W}_j^{(00)}(s,s) ,$$

$$\epsilon_1 = \tfrac{1}{2} \sum_{i>j} [\overleftrightarrow{W}_i^{(00)}(s,s) \cdot \overleftrightarrow{W}_j^{(00)}(p,p)$$

$$+ \overleftrightarrow{W}_i^{(00)}(p,p) \cdot \overleftrightarrow{W}_j^{(00)}(s,s)] ,$$

$$\epsilon_2 = \tfrac{1}{2} \sum_{i>j} \overleftrightarrow{W}_i^{(00)}(p,p) \cdot \overleftrightarrow{W}_j^{(00)}(p,p) , \tag{1}$$

$$\epsilon_3 = \tfrac{1}{2} \sum_{i>j} \overleftrightarrow{W}_i^{(02)}(p,p) \cdot \overleftrightarrow{W}_j^{(02)}(p,p) ,$$

$$\epsilon_4 = \tfrac{1}{2} \sum_{i>j} [\overleftrightarrow{W}_i^{(01)}(s,p) - \overleftrightarrow{W}_i^{(01)}(p,s)]$$

$$\cdot [\overleftrightarrow{W}_j^{(01)}(s,p) - \overleftrightarrow{W}_j^{(01)}(p,s)] .$$

Thus, we find

$$H = 4F_0(ss)\epsilon_0 + 12F_0(pp)\epsilon_2 + 4\sqrt{3}F_0(sp)\epsilon_1$$

$$+ 24F_2(pp)\epsilon_3 + 4G_1(sp)\epsilon_4 .$$

The next step is to express the R_4 tensors in terms of ϵ_i. We represent $[(00) \times (00)]^{(00)}$, $[(00) \times (20)]^{(20)}$, $[(20) \times (20)]^{(00)}$, $[(20) \times (20)]^{(20)}$, and $[(20) \times (20)]^{(40)}$ by e_0, e_1, e_2, e_3, and e_4, respectively. Then, by using the Wigner coefficients for the reduction of $R_4 \times R_4$, we have

$$e_0 = \tfrac{1}{2}(\epsilon_0 + \sqrt{3}\epsilon_1 + 3\epsilon_2) ,$$

$$e_1 = \tfrac{1}{2}(\sqrt{3}\epsilon_0 + \epsilon_1 - \sqrt{3}\epsilon_2) ,$$

$$e_2 = \tfrac{1}{6}(3\epsilon_0 - \sqrt{3}\epsilon_1 + \epsilon_2) - \tfrac{1}{3}\epsilon_4 + \tfrac{2}{3}\epsilon_3 , \tag{2}$$

$$e_3 = \tfrac{1}{6}\sqrt{3}(3\epsilon_0 - \sqrt{3}\epsilon_1 + \epsilon_2) - \tfrac{1}{6}\sqrt{3}\epsilon_4 - \tfrac{1}{3}\sqrt{3}\epsilon_3 ,$$

$$e_4 = \tfrac{1}{6}\sqrt{5}(3\epsilon_0 - \sqrt{3}\epsilon_1 + \epsilon_2) + \tfrac{1}{6}\sqrt{5}\epsilon_4 + \tfrac{1}{15}\sqrt{5}\epsilon_3 .$$

Inverting Eqs. (2) and inserting the result in (1), one finds

$$H = \sum_{i=0}^{4} e_i E_i ,$$

where

$$E_0 = 2F_0(ss) + 12F_0(sp) + 18F_0(pp) ,$$

$$E_1 = \sqrt{3}[4F_0(ss) + 8F_0(sp) - 12F_0(pp)] ,$$

$$E_2 = 2F_0(ss) - 4F_0(sp) + 2F_0(pp) + 80F_2(pp)$$
$$- 16G_1(sp) ,$$

$$E_3 = \sqrt{3}[2F_0(ss) - 4F_0(sp) + 2F_0(pp) - 40F_2(pp)$$
$$- 8G_1(sp)] ,$$

$$E_4 = \sqrt{5}[2F_0(ss) - 4F_0(sp) + 2F_0(pp) + 8F_2(pp)$$
$$+ 8G_1(sp)] .$$

Putting in hydrogenic values for the Slater integrals, one finds that none of the E_i vanish. The same result follows by looking at the E_i given by Feneuille[5] for $(s+d)^N$ configurations. That some of the E_i are small compared to others is not significant, because this is partly an expression of the fact that F_k and G_k decrease rapidly as k increases; moreover, it is the differences between the various Slater integrals that are important: otherwise, to a first approximation, $F_0(ss)$, $F_0(sp)$, and $F_0(pp)$ are equal. Differences between individual elements of an energy matrix, even when much smaller than the trace, have a profound significance, because the trace leads only to an energy shift, whereas it is precisely the differences that yield a splitting of the levels.

A complete analysis for the $n=3$ shell in terms of R_9 tensors e_i would proceed analogously. The Coulomb Hamiltonian would first have to be written as in Eq. (1) in terms of the ϵ_i and the 17 Slater integrals. Reference 2 considers only 14 two-electron integrals. While it is true that there are 14 F's and G's, what is relevant is to consider all independent two-electron integrals, including the $3R^k(ab, cd)$ which cannot be cast as F's and G's because three of the four orbitals are different.

On the question of the number of independent parameters, the point to be emphasized is this: Is it sufficient to just consider (000), (200), and (400), as in Ref. 2 or should one also look at how these arise from the "single-particle" tensors as in this comment? This is analogous to saying: Is it enough to say F^0, or should one differentiate between $F^0(ss)$ and $F^0(pp)$? The point of this comment is that differences between such R^k of same k, though of the order of 15–25%, are central to Slater integrals. Since the results of Ref. 2 agree with the exact values only to this accuracy, there is not sufficient evidence to ascribe any physical significance to the "physical" description[2] of R_4.

While this paper was being written, Dr. B. G. Wybourne kindly informed us that he and P. H.

Butler have come to very similar conclusions during the course of a general study of R_4 and electron correlations for $(s+p)^N$ configurations. Their results will be published shortly.[7] These authors also have an explanation for the sign reversals in Refs. 1 and 2.

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Two Uses of R_4 in the Study of Atomic Structure

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The two different uses of R_4, one as a mathematical and one as physical group which were discussed in previous work, are presented. The treatment of Rau is shown to be equivalent to the mathematical approach. The use of the physical group leads to new relationships not present in the mathematical approach.

In his thesis this writer[1] derived some results applying the four-dimensional rotation group to atomic structure theory. Two different uses of R_4 were contrasted. These approaches were characterized as the "mathematical" description[2] and the "physical" description of R_4. The mathematical R_4 originated in the work of Racah,[3] who realized that the angular parts of the set of $(2l+1)$ orbitals of orbital angular momentum l transform in the same way as the generators of R_{2l+1}. We have called this use of the group the mathematical description because Racah made use of the group only to simplify the mathematical analysis of complex configurations; he attributed no physical significance to the group. Later, it was realized that the angular parts of the set of $2l+1+2l'+1$ orbitals of angular momentum l and l' transform like the generators of $R_{2l+2l'+2}$. Again, no physical significance was found for these transformation properties.

The physical R_4, on the other hand, does have physical significance; it is a different R_4. It is well known that the hydrogen atom possesses R_4 symmetry exactly. It is found that the Fourier transform of the hydrogen atom wave functions transforms according to representations of R_4.

It must be emphasized that we are dealing with the entire wave function and not the angular parts alone. In our previous work we attempted to extend this physical use of R_4 to atoms other than hydrogen, in particular the first-row atoms, in the hope that R_4 would be an approximate symmetry group for these atoms.

To accomplish this end for the $2s^m2p^n$ configurations, we expressed all the relevant two-electron wave functions in terms of tensors transforming according to irreducible representations of R_4. Again, we emphasize that we treat the entire wave functions and not just the angular parts. We then expressed the Coulomb operator in terms of R_4 tensors and found that we required three parameters rather than the five F and G parameters required if R_4 symmetry is not invoked. We then determined these parameters and found that we could determine the five F and G parameters from these three parameters quite accurately, thus justifying our use of R_4 as an approximate symmetry group for the first-row atoms.

In a recent paper, Rau[4] finds that it is not possible to reduce the number of parameters in the Coulomb interaction to three. An analysis of his