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$O(4)$ and $U(3)$ Symmetry Breaking in the $2s$-$2p$ Shell

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A group-theoretical analysis of the states of first-row atoms and their internal electrostatic interactions is developed. The Hamiltonian is found to be completely expressible as a linear combination of operators that are diagonal in $U(3)$, operators diagonal in $O(4)$, and operators diagonal in both. This makes possible a simple and uniform treatment of the energy levels of first-row atoms. We use it here to analyze configuration mixing between the $2s^2 2p^x$ and $2p^{x+2}$ configurations, and determine the contribution of configurations of $O(4)$ and $U(3)$ symmetry in several types of mixed-configuration wave functions.

I. INTRODUCTION

It has been well known since the work of Fock[1] and of Bargmann[2] that the accidental degeneracy of the energy levels of a particle in a Coulomb potential is due to the fact that the problem has as a symmetry group the orthogonal group of four dimensions $O(4)$. This group contains as a subgroup the usual proper orthogonal group in three dimensions $O^+(3)$, associated with rotations in the physical space. Thus, the Coulomb problem has a higher symmetry than the one associated with an arbitrary central potential.

The group $O(4)$ continues to be a symmetry group when we pass from 1 to Z noninteracting particles in a Coulomb potential. The question that immediately arises is: To what extent will the symmetry continue to hold when we introduce a Coulomb interaction between the particles? If the symmetry is only weakly broken, the $O(4)$ group would provide us with new approximate integrals of motion, i.e., new quantum numbers, for the atomic Hamiltonian, at least insofar as we neglect any spin-dependent contribution to this Hamiltonian. On the other hand, if the symmetry is not retained in the presence of the interaction, it is interesting to determine the manner of symmetry breaking for the states that are the basis for irreducible representations (IR) of $O(4)$.

We shall analyze in this paper the $O(4)$ symmetry breaking for a system of electrons that are filling the $2s$-$2p$ shell of the common Coulomb potential when we introduce an interaction between the electrons. We shall also see that the states in the $2s$-$2p$ shell can be classified according to the IR of a $U(3)$ group, which essentially gives the distribution of the electrons between the $2s$ and the $2p$ shells. We then discuss the symmetry breaking introduced by the interaction between the electrons in the $U(3)$ classification scheme. Furthermore, we later take into account the effect of the closed $1s$ shell when the states are classified by the IR either of $O(4)$ or of $U(3)$.

We shall compare the results of our analysis with the Hartree-Fock calculations of other authors, thus being able to give a quantitative measure to the extent of symmetry breaking both in the $O(4)$ and $U(3)$ cases.

We start our discussion with the introduction of the classification schemes for the states in the $2s$-$2p$ shell.

II. CLASSIFICATION SCHEMES IN $2s$-$2p$ SHELL ASSOCIATED WITH IRREDUCIBLE REPRESENTATIONS OF $U(3)$ or $O(4)$

Consider the states in the $2s$-$2p$ shells of a common Coulomb potential for a system of n particles. The states admit the following integrals of motion, which will remain good even in the presence of a central interaction: the total number of particles n in the $2s$-$2p$ shell, the total spin S and its projection M_S, the total orbital angular momentum L and its projection M_L, and the parity π. Further quantum numbers are in general necessary to completely characterize the states. We consider first configurations that can be denoted $(2s)^d\ (2p)^{n-d}$, where d is the number of electrons in the $2s$ subshell. The states can then be characterized by the kets

$$|(2s)^d (2p)^{n-d} S M_S L M_L \pi\rangle \equiv |nSL^\pi d\rangle\ . \qquad (2.1)$$

We shall denote these states by the shorthand notation on the right-hand side of (2.1), where M_S and M_L have been suppressed, as they are irrelevant for calculation with central interactions. The kets (2.1) contain no other quantum numbers, as in the $2s$-$2p$ shell n, d with S, L, and π completely characterize the states, as discussed in Appendix A.

We also show in Appendix A that the kets (2.1) are characterized by the IR of a unitary group in three dimensions $U(3)$ associated with the $2p$ subshell.

In Tables I and II we give all possible values for n, S, L, π, and d for states with $n = 0, 1, \ldots, 8$ particles. We have separated the states into two sets. The first set is in Table I, where n, S, L, π by itself characterizes the state; i.e., there is only one state for these quantum numbers. The second set is given in Table II, where we have two states for each n, S, L, π. This distribution is convenient for the presentation of the two-body matrix elements discussed in Sec. II, which are also given in Tables I and II. There are seven pairs of states in Table II. Each pair of states of a given n, S, L, π has been termed a "complex" by Layzer and we shall use this term henceforth.[3]

In the column after the d we include the IR of $U(3)$ characterized by the partition $(h_1h_2h_3)$ of $n-d$. We note that there is a one-to-one correspondence between $(h_1h_2h_3)$ and d, once the quantum numbers n, S, L, and π are specified.

As is well known, the Coulomb problem admits, besides the angular momentum $\vec{L}' = \vec{r}\times\vec{p}$, another integral of motion, the Runge-Lenz vector

$$\vec{A}' = (2Zme^2)^{-1}(\vec{L}'\times\vec{p} - \vec{p}\times\vec{L}') + (1/r)\vec{r}\ . \qquad (2.2)$$

Both $\vec{L}'$ and $\vec{A}'$ commute then with the Hamiltonian

$$\mathcal{H} = p^2/2m - Ze^2/r\ . \qquad (2.3)$$

We redefine now the angular momenta and Runge-Lenz vector by

$$\vec{L} = \frac{1}{\hbar}\vec{L}'\,, \qquad \vec{A} = \left(-\frac{2\hbar^2}{Z^2me^4}\mathcal{H}\right)^{-1/2}\vec{A}' \qquad (2.4)$$

and find that the commutation relations between the two vectors are

$$\begin{aligned} [L_j,\ L_k] &= i\epsilon_{jkl}L_l\,, \\ [L_j,\ A_k] &= i\epsilon_{jkl}A_l\,, \qquad (2.5) \\ [A_j,\ A_k] &= i\epsilon_{jkl}L_l\,, \end{aligned}$$

which are associated with a Lie algebra[2] of an orthogonal group of four dimensions $O(4)$. This group

Table I. One-component states of the L shell.

nSL^{π}	$(h_1h_2h_3)d$	$(\mu\nu)$	Numerical eigenvalue of interaction $\sum_{i>j} e^2/r_{ij}$ for hydrogenic basis	Eigenvalue of interaction $\sum_{i>j} V(r_{ij})$ in terms of Slater integrals[a]
$1\frac{1}{2}1^-$	(100)0	$(\frac{1}{2}\frac{1}{2})$	0	0
$1\frac{1}{2}0^+$	(000)1	$(\frac{1}{2}\frac{1}{2})$	0	0
202^+	(200)0	(11)	$(Z'e^2/512a_0)$ (94.8)	$F^0_{11}+\frac{1}{25}F^2_{11}$
201^-	(100)1	(11)	$(Z'e^2/512a_0)$ (98)	$F^0_{01}+\frac{1}{3}G^1_{01}$
211^+	(110)0	(10)	$(Z'e^2/512a_0)$ (84)	$F^0_{11}-\frac{1}{5}F^2_{11}$
211^-	(100)1	(10)	$(Z'e^2/512a_0)$ (68)	$F^0_{01}-\frac{1}{3}G^1_{01}$
$3\frac{1}{2}2^-$	(210)0	$(\frac{3}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (268.2)	$3F^0_{11}-\frac{6}{25}F^2_{11}$
$3\frac{1}{2}0^+$	(200)1	$(\frac{1}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (262)	$2F^0_{01}-\frac{1}{3}G^1_{01}+F^0_{11}+\frac{2}{5}F^2_{11}$
$3\frac{1}{2}1^+$	(110)1	$(\frac{3}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (265)	$2F^0_{01}+\frac{1}{3}G^1_{01}+F^0_{11}-\frac{1}{5}F^2_{11}$
$3\frac{1}{2}2^+$	(200)1	$(\frac{3}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (245.8)	$2F^0_{01}-\frac{1}{3}G^1_{01}+F^0_{11}+\frac{1}{25}F^2_{11}$
$3\frac{3}{2}0^-$	(111)0	$(\frac{1}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (252)	$3F^0_{11}-\frac{3}{5}F^2_{11}$
$3\frac{3}{2}1^-$	(110)1	$(\frac{1}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (220)	$2F^0_{01}-\frac{2}{3}G^1_{01}+F^0_{11}-\frac{1}{5}F^2_{11}$
401^-	(210)1	(11)	$(Z'e^2/512a_0)$ (528)	$3F^0_{01}+3F^0_{11}$
402^-	(210)1	(20)	$(Z'e^2/512a_0)$ (517.2)	$3F^0_{01}+3F^0_{11}-\frac{6}{25}F^2_{11}$
411^-	(210)1	(10)	$(Z'e^2/512a_0)$ (498)	$3F^0_{01}-\frac{2}{3}G^1_{01}+3F^0_{11}$
410^-	(111)1	(11)	$(Z'e^2/512a_0)$ (516)	$3F^0_{01}+\frac{1}{3}G^1_{01}+3F^0_{11}-\frac{3}{5}F^2_{11}$
412^-	(210)1	(11)	$(Z'e^2/512a_0)$ (487.2)	$3F^0_{01}-\frac{2}{3}G^1_{01}+3F^0_{11}-\frac{6}{25}F^2_{11}$
420^-	(111)1	(00)	$(Z'e^2/512a_0)$ (456)	$3F^0_{01}-G^1_{01}+3F^0_{11}-\frac{3}{5}F^2_{11}$
$5\frac{1}{2}2^-$	(210)2	$(\frac{3}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (798.2)	$F^0_{00}+6F^0_{01}-G^1_{01}+3F^0_{11}-\frac{6}{25}F^2_{11}$
$5\frac{1}{2}0^+$	(220)1	$(\frac{1}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (860)	$4F^0_{01}-\frac{2}{3}G^1_{01}+6F^0_{11}$
$5\frac{1}{2}1^+$	(211)1	$(\frac{3}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (863)	$4F^0_{01}+6F^0_{11}-\frac{3}{5}F^2_{11}$
$5\frac{1}{2}2^+$	(220)1	$(\frac{3}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (843.8)	$4F^0_{01}-\frac{2}{3}G^1_{01}+6F^0_{11}-\frac{9}{25}F^2_{11}$
$5\frac{3}{2}0^-$	(111)2	$(\frac{1}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (782)	$F^0_{00}+6F^0_{01}-G^1_{01}+3F^0_{11}-\frac{3}{5}F^2_{11}$
$5\frac{3}{2}1^+$	(211)1	$(\frac{1}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (818)	$4F^0_{01}-G^1_{01}+6F^0_{11}-\frac{3}{5}F^2_{11}$
602^+	(220)2	(11)	$(Z'e^2/512a_0)$ (1222.8)	$F^0_{00}+8F^0_{01}-\frac{4}{3}G^1_{01}+6F^0_{11}-\frac{9}{25}F^2_{11}$
601^-	(221)1	(11)	$(Z'e^2/512a_0)$ (1294)	$5F^0_{01}+10F^0_{11}-\frac{4}{5}F^2_{11}-\frac{1}{3}G^1_{01}$
611^+	(211)2	(10)	$(Z'e^2/512a_0)$ (1212)	$F^0_{00}+8F^0_{01}-\frac{4}{3}G^1_{01}+6F^0_{11}-\frac{3}{5}F^2_{11}$
611^-	(221)1	(10)	$(Z'e^2/512a_0)$ (1264)	$5F^0_{01}-G^1_{01}+10F^0_{11}-\frac{4}{5}F^2_{11}$
$7\frac{1}{2}1^-$	(221)2	$(\frac{1}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (1726)	$F^0_{00}+10F^0_{01}-\frac{5}{3}G^0_{01}+10F^0_{11}-\frac{4}{5}F^2_{11}$
$7\frac{1}{2}0^+$	(222)1	$(\frac{1}{2}\frac{1}{2})$	$(Z'e^2/512a_0)$ (1794)	$6F^0_{01}-G^0_{01}+15F^0_{11}-\frac{6}{5}F^2_{11}$
800^+	(222)2	(00)	$(Z'e^2/512a_0)$ (2324)	$F^0_{00}+12F^0_{01}+15F^0_{11}-\frac{6}{5}F^2_{11}-2G^1_{01}$

[a] In F^k_{ii} and G^k_{ii}, $i=0$ denotes $2s$, $i=1$ denotes $2p$; e.g., $G^1_{01}=G^1_{(2s2p)}$.

TABLE II. $U(3)$ matrices.

nSL^{π}	$(h_1h_2h_3)d$	Numerical matrices for the interaction	Matrices for interaction $\sum_{i>j} V(r_{ij})$ in terms of Slater integrals
200^+	(200)0 (000)2	$\frac{Z'e^2}{512a_0}\begin{pmatrix} 111 & -15\sqrt{3} \\ -15\sqrt{3} & 77 \end{pmatrix}$	$\begin{pmatrix} F^0_{11}+\frac{2}{5}F^2_{11} & -(1/\sqrt{3})G^1_{10} \\ -(1/\sqrt{3})G^1_{10} & F^0_{00} \end{pmatrix}$
$3\frac{1}{2}1^-$	(210)0 (100)2	$\frac{Z'e^2}{512a_0}\begin{pmatrix} 279 & -15\sqrt{2} \\ -15\sqrt{2} & 228 \end{pmatrix}$	$\begin{pmatrix} 3F^0_{11} & -(2\sqrt{2}/9)G^1_{10} \\ -(2\sqrt{2}/9)G^1_{10} & F^0_{00}-\frac{1}{3}G^1_{10}+2F^0_{01} \end{pmatrix}$
400^+	(220)0 (200)2	$\frac{Z'e^2}{512a_0}\begin{pmatrix} 558 & -30 \\ -30 & 490 \end{pmatrix}$	$\begin{pmatrix} 6F^0_{11} & -\frac{2}{3}G^1_{10} \\ -\frac{2}{3}G^1_{10} & F^0_{00}+4F^0_{01}-\frac{2}{3}G^1_{10}+F^0_{11}+\frac{2}{5}F^2_{11} \end{pmatrix}$
402^+	(220)0 (200)2	$\frac{Z'e^2}{512a_0}\begin{pmatrix} 541.8 & -15 \\ -15 & 473.8 \end{pmatrix}$	$\begin{pmatrix} 6F^0_{11}-\frac{9}{25}F^2_{11} & -\frac{1}{3}G^1_{10} \\ -\frac{1}{3}G^1_{10} & F^0_{00}+4F^0_{01}-\frac{2}{3}G^1_{10}+F^0_{11}+\frac{1}{25}F^2_{11} \end{pmatrix}$
411^+	(211)0 (110)2	$\frac{Z'e^2}{512a_0}\begin{pmatrix} 531 & 15 \\ 15 & 463 \end{pmatrix}$	$\begin{pmatrix} 6F^0_{11}-\frac{3}{5}F^2_{11} & \frac{1}{3}G^1_{10} \\ \frac{1}{3}G^1_{10} & F^0_{00}+4F^0_{01}-\frac{2}{3}G^1_{10}+F^0_{11}-\frac{1}{5}F^2_{11} \end{pmatrix}$
$5\frac{1}{2}1^-$	(221)0 (210)2	$\frac{Z'e^2}{512a_0}\begin{pmatrix} 894 & 15\sqrt{2} \\ 15\sqrt{2} & 809 \end{pmatrix}$	$\begin{pmatrix} 10F^0_{11}-\frac{4}{5}F^2_{11} & (\sqrt{2}/3)G^1_{10} \\ (\sqrt{2}/3)G^1_{10} & F^0_{00}+6F^0_{01}-G^1_{10}+3F^0_{11} \end{pmatrix}$
600^+	(222)0 (220)2	$\frac{Z'e^2}{512a_0}\begin{pmatrix} 1341 & 15\sqrt{3} \\ 15\sqrt{3} & 1239 \end{pmatrix}$	$\begin{pmatrix} 15F^0_{11}-\frac{6}{5}F^2_{11} & (1/\sqrt{3})G^1_{10} \\ (1/\sqrt{3})G^1_{10} & F^0_{00}+8F^0_{01}-\frac{4}{3}G^1_{10}+6F^0_{11} \end{pmatrix}$

contains a subgroup, the proper orthogonal group of three dimensions $O^+(3)$ associated with ordinary rotations whose generators are L.

We could then try to characterize the set of states in the $2s$-$2p$ shell by IR of the $O(4)$ group. For this we are required first to know the quantum numbers that could characterize the IR of $O(4)$. There are many ways of defining them, but one we find particularly transparent involves the introduction of the two auxiliary vectors[4]

$$\vec{\mathfrak{M}}=\tfrac{1}{2}(\vec{L}+\vec{A}),\quad \vec{\mathfrak{N}}=\tfrac{1}{2}(\vec{L}-\vec{A}), \tag{2.6}$$

which from (2.5) satisfy the commutation relations

$$[\mathfrak{M}_j,\mathfrak{M}_k]=i\epsilon_{jkl}\mathfrak{M}_l,\quad [\mathfrak{N}_j,\mathfrak{N}_k]=i\epsilon_{jkl}\mathfrak{N}_l,\quad [\mathfrak{M}_j,\mathfrak{N}_k]=0. \tag{2.7}$$

The new generators $\mathfrak{M}_i$ and $\mathfrak{N}_j$ of $O(4)$ show then explicitly that this group is locally isomorphic to the direct product of two three-dimensional orthogonal groups. The IR of this group are determined by the eigenvalues of the operators $\vec{\mathfrak{M}}^2$ and $\vec{\mathfrak{N}}^2$, which we could denote, respectively, by $\mu(\mu+1)$ and $\nu(\nu+1)$.

We shall then characterize the IR of our $O(4)$ group by the two numbers

$$(\mu,\ \nu). \tag{2.8}$$

As from (2.6), $\vec{L}=\vec{\mathfrak{M}}+\vec{\mathfrak{N}}$, we conclude that

$$|\mu-\nu|\leq L\leq \mu+\nu \tag{2.9}$$

and, moreover, either both μ and ν are integer or both are semi-integer. The states in the $2s$-$2p$ shell can then also be denoted by

$$|nSL^{\pi}(\mu\nu)\rangle. \tag{2.10}$$

When dealing with the problem of a single particle in the Coulomb potential, i.e., when $\vec{L}$ and $\vec{A}$ are given by (2.4), it is obvious that $\vec{A}\cdot\vec{L}=0$ and thus $\vec{\mathfrak{M}}^2=\vec{\mathfrak{N}}^2$. Single-particle states are then characterized by the IR $(\mu\mu)$ of $O(4)$, and it can be easily shown[2,4] that

$$\begin{aligned}\mathcal{H}&=-(Z^2m^2e^4/2\hbar^2)(2\mathfrak{M}^2+2\mathfrak{N}^2+1)^{-1}\\ &=-(Z^2m^2e^4/2\hbar^2)(4\mathfrak{M}^2+1)^{-1}.\end{aligned} \tag{2.11}$$

We conclude that

$$4\mu(\mu+1)+1=(2\mu+1)^2 \tag{2.12}$$

corresponds to the square of the principal quantum number. Thus the $1s$ shell corresponds to $\mu=0$, the $2s$-$2p$ shell to $\mu=\frac{1}{2}$, the $3s$-$3d$ shell to $\mu=1$, etc. In particular, in our shell of interest the single-particle states could be characterized by

$$(\mu\nu)LM=(\tfrac{1}{2}\tfrac{1}{2})00\quad\text{or}\quad(\tfrac{1}{2}\tfrac{1}{2})1M, \tag{2.13}$$

the first corresponding to $2s$ and the second to $2p$.

The states from 0 to 8 particles in the $2s$-$2p$ shell can then be built from the single-particle states (2.13) by using the standard rules of addition of angular momenta for $\vec{\mathfrak{M}}$ and $\vec{\mathfrak{N}}$ separately, as well as for their sum $\vec{L}$, thus obtaining the values of the quantum numbers $(\mu\nu)L$ appearing in the ket (2.10).

In Tables I and III we give the values of $(\mu\nu)$ for the IR of $O(4)$ associated with the states characterized by n, S, L, π. As in the case of $U(3)$, we separate our states into two sets, the first in Table I, where there is only one state for each n, S, L, π, and the second in Table III, where there are two states for these quantum numbers. The seven 2×2 matrices that connect the states in the $O(4)$ with the states in the $U(3)$ classification are given in Table IV.

The group-theoretical background on which these tables are based is discussed in detail in Appendix A. There we show that the states in the $2s$-$2p$ shell are characterized by the completely antisymmetric IR $[1^n]$ of a unitary group whose dimensions are equal to the total number of single-particle states in the $2s$-$2p$ shell, i.e., $U(8)$. Furthermore, this group admits as a subgroup the direct product of a unitary group of four dimensions $U(4)$ associated with the configuration part of the states and a unitary unimodular group $SU^\sigma(2)$ associated with the spin part, i.e.,

$$U(8)\supset U(4)\times SU^\sigma(2)\,. \tag{2.14}$$

The group $U(4)$ can admit several chains of subgroups, two of which are of particular interest to us. The first one contains a unitary group in three dimensions associated with the $2p$ subshell, and the second the orthogonal group in four dimensions. Both chains contain as a subgroup the proper orthogonal group of three dimensions $O^+(3)$ associated with rotations in ordinary space, i.e.,

$$U(4)\supset \begin{pmatrix} U(3) & 0\\ 0 & 1\end{pmatrix}\supset \begin{pmatrix} O^+(3) & 0\\ 0 & 1\end{pmatrix}, \tag{2.15a}$$

$$U(4)\supset O(4)\supset \begin{pmatrix} O^+(3) & 0\\ 0 & 1\end{pmatrix}. \tag{2.15b}$$

The quantum numbers appearing in the ket (2.1) are related to the IR of the groups in the chain (2.14), (2.15a), while those in the ket (2.10) are related to the chain (2.14), (2.15b). Thus, for example, in (2.10) n, S, L, π, and $(\mu\nu)$ are related, respectively, with the IR of $U(8)$, $SU^\sigma(2)$,$O^+(3)$, and $O(4)$. The IR of $U(4)$ is dependent on n and S, as indicated in Appendix A.

By using well-known branching rules[5] of the unitary and orthogonal groups, all the possible quantum numbers in Tables I and II were obtained, as well as the explicit form of the kets (2.1). By determining the matrices of $\vec{A}^2=2\vec{\mathfrak{M}}^2+2\vec{\mathfrak{N}}^2-\vec{L}^2$ with respect to the kets (2.1) for the seven two-dimensional cases, and then diagonalizing them, we get the remaining states (2.10), and thus the matrices given in Table IV.

When using $\vec{A}$ it is not necessary to assume that one is dealing with hydrogenic functions and that it is expressed in terms of the dynamical variables as indicated by (2.2) and (2.4). One may define a general $\vec{A}$ by the matrix elements of one of its components and the commutation relations (2.5). We choose the defining elements to be

$$A_0|2s\rangle=|2p_0\rangle,\qquad A_0|2p_0\rangle=|2s\rangle\,. \tag{2.16}$$

We assume the Condon-Shortley phase conventions.

TABLE III. $O(4)$ matrices.

nSL^π	$(\mu\nu)$	Numerical matrices for the interaction $\sum_{i>j} e^2/r_{ij}$	Matrices for interaction $\sum_{i<j} V(r_{ij})$ in terms of Slater integrals
200^+	(00) (11)	$\frac{Z'e^2}{512a_0}\begin{pmatrix}80 & -16\sqrt{3}\\ -16\sqrt{3} & 108\end{pmatrix}$	$\begin{pmatrix}\frac{3}{4}F^0_{11}+\frac{1}{4}F^0_{00}+\frac{3}{10}F^2_{11}-\frac{1}{2}G^1_{10} & -(\sqrt{3}/4)F^0_{11}+(\sqrt{3}/4)F^0_{00}-(\sqrt{3}/10)F^2_{11}-(\sqrt{3}/6)G^1_{10}\\ -\text{ to get }-(\sqrt{3}/4)F^0_{11}+(\sqrt{3}/4)F^0_{00}-(\sqrt{3}/10)F^2_{11}-(\sqrt{3}/6)G^1_{10} & \frac{1}{4}F^0_{11}+\frac{3}{4}F^0_{00}+\frac{1}{10}F^2_{11}+\frac{1}{2}G^1_{10}\end{pmatrix}$
$3\frac{1}{2}1^-$	$(\frac{1}{2}\,\frac{1}{2})$	$\frac{Z'e^2}{512a_0}\begin{pmatrix}242 & -22\sqrt{2}\\ -22\sqrt{2} & 265\end{pmatrix}$	$\begin{pmatrix}\frac{1}{3}F^0_{00}+\frac{2}{3}F^0_{01}+2F^0_{11}-\frac{11}{27}G^1_{10} & (\sqrt{2}/3)F^0_{00}+(2\sqrt{2}/3)F^0_{01}-\sqrt{2}F^0_{11}-(5\sqrt{2}/27)G^1_{10}\\ (\sqrt{2}/3)F^0_{00}+(2\sqrt{2}/3)F^0_{01}-\sqrt{2}F^0_{11}-(5\sqrt{2}/27)G^1_{10} & \frac{2}{3}F^0_{00}+\frac{4}{3}F^0_{01}+F^0_{11}+\frac{2}{27}G^1_{10}\end{pmatrix}$
400^+	(00) (11)	$\frac{Z'e^2}{512a_0}\begin{pmatrix}494 & -34\\ -34 & 554\end{pmatrix}$	$\begin{pmatrix}\frac{1}{2}F^0_{00}+2F^0_{01}+\frac{7}{2}F^0_{11}+\frac{1}{5}F^2_{11}-G^1_{10} & \frac{1}{2}F^0_{00}+2F^0_{01}-\frac{5}{2}F^0_{11}+\frac{1}{5}F^2_{11}-\frac{1}{3}G^1_{10}\\ \frac{1}{2}F^0_{00}+2F^0_{01}-\frac{5}{2}F^0_{11}+\frac{1}{5}F^2_{11}-\frac{1}{3}G^1_{10} & \frac{1}{2}F^0_{00}+2F^0_{01}+\frac{7}{2}F^0_{11}+\frac{1}{5}F^2_{11}+\frac{1}{3}G^1_{10}\end{pmatrix}$
402^+	(11) (10)	$\frac{Z'e^2}{512a_0}\begin{pmatrix}492.8 & -34\\ -34 & 522.8\end{pmatrix}$	$\begin{pmatrix}\frac{1}{2}F^0_{00}+2F^0_{01}+\frac{7}{2}F^0_{11}-\frac{4}{25}F^2_{11}-\frac{2}{3}G^1_{10} & \frac{1}{2}F^0_{00}+2F^0_{01}-\frac{5}{2}F^0_{11}+\frac{1}{5}F^2_{11}-\frac{1}{3}G^1_{10}\\ \frac{1}{2}F^0_{00}+2F^0_{01}-\frac{5}{2}F^0_{11}+\frac{1}{5}F^2_{11}-\frac{1}{3}G^1_{10} & \frac{1}{2}F^0_{00}+2F^0_{01}+\frac{7}{2}F^0_{11}-\frac{4}{25}F^2_{11}\end{pmatrix}$
411^+	(11) (20)	$\frac{Z'e^2}{512a_0}\begin{pmatrix}512 & -34\\ -34 & 482\end{pmatrix}$	$\begin{pmatrix}\frac{1}{2}F^0_{00}+2F^0_{01}+\frac{7}{2}F^0_{11}-\frac{2}{5}F^2_{11} & \frac{1}{2}F^0_{00}+2F^0_{01}-\frac{5}{2}F^0_{11}+\frac{1}{5}F^2_{11}-\frac{1}{3}G^1_{10}\\ \frac{1}{2}F^0_{00}+2F^0_{01}-\frac{5}{2}F^0_{11}+\frac{1}{5}F^2_{11}-\frac{1}{3}G^1_{10} & \frac{1}{2}F^0_{00}+2F^0_{01}+\frac{7}{2}F^0_{11}-\frac{2}{5}F^2_{11}-\frac{2}{3}G^1_{10}\end{pmatrix}$
$5\frac{1}{2}1^-$	$(\frac{1}{2}\frac{1}{2})$ $(\frac{3}{2}\,\frac{1}{2})$	$\frac{Z'e^2}{512a_0}\begin{pmatrix}817.3 & 23.3\sqrt{2}\\ 23.3\sqrt{2} & 885.7\end{pmatrix}$	$\begin{pmatrix}\frac{2}{3}F^0_{00}+4F^0_{01}+\frac{16}{3}F^0_{11}-\frac{4}{15}F^2_{11}-\frac{10}{9}G^1_{10} & -(\sqrt{2}/3)\;{}^{0}_{00}-2\sqrt{2}F^0_{01}+(7\sqrt{2}/3)F^0_{11}-(4\sqrt{2}/15)F^2_{11}+(2\sqrt{2}/9)G^1_{10}\\ -(\sqrt{2}/3)F^0_{00}-2\sqrt{2}F^0_{01}+(7\sqrt{2}/3)F^0_{11}-4\sqrt{2}/15)F^2_{11}+(2\sqrt{2}/9)G^1_{10} & \frac{1}{3}F^0_{00}+2F^0_{01}+\frac{23}{3}F^0_{11}-\frac{8}{15}F^2_{11}+\frac{1}{9}G^1_{10}\end{pmatrix}$
600^+	(00) (11)	$\frac{Z'e^2}{512a_0}\begin{pmatrix}1242 & 18\sqrt{3}\\ 18\sqrt{3} & 1338\end{pmatrix}$	$\begin{pmatrix}\frac{3}{4}F^0_{00}+6F^0_{01}+\frac{33}{4}F^0_{11}-\frac{3}{10}F^2_{11}-\frac{3}{2}G^1_{10} & -(\sqrt{3}/4)F^0_{00}-2\sqrt{3}F^0_{01}+(9\sqrt{3}/4)F^0_{11}-(3\sqrt{3}/10)F^2_{11}+(\sqrt{3}/6)G^1_{10}\\ (\sqrt{3}/4)F^0_{00}-2\sqrt{3}F^0_{01}+(9\sqrt{3}/4)F^0_{11}-(3\sqrt{3}/10)F^2_{11}+(\sqrt{3}/6)G^1_{10} & \frac{1}{4}F^0_{00}+2F^0_{01}+\frac{51}{4}F^0_{11}-\frac{9}{10}F^2_{11}+\frac{1}{6}G^1_{10}\end{pmatrix}$

TABLE IV. Transformation matrices between $U(4) \supset U(3)$ and $U(4) \supset O(4)$ chains.

nSL^π	A^2	$(\mu\nu)$ ^{d}	0	2
200^+	0	(00)	$\sqrt{3}/2$	$\frac{1}{2}$
	8	(11)	$-\frac{1}{2}$	$\sqrt{3}/2$
$3\frac{1}{2}1^-$	1	$(\frac{1}{2}\frac{1}{2})$	$\sqrt{\frac{2}{3}}$	$1/\sqrt{3}$
	7	$(\frac{3}{2}\frac{1}{2})$	$-1/\sqrt{3}$	$\sqrt{\frac{2}{3}}$
400^+	0	(00)	$1/\sqrt{2}$	$1/\sqrt{2}$
	8	(11)	$-1/\sqrt{2}$	$1/\sqrt{2}$
402^+	2	(11)	$1/\sqrt{2}$	$1/\sqrt{2}$
	6	(20)	$-1/\sqrt{2}$	$1/\sqrt{2}$
411^+	6	(11)	$1/\sqrt{2}$	$1/\sqrt{2}$
	2	(10)	$-1/\sqrt{2}$	$1/\sqrt{2}$
$5\frac{1}{2}1^-$	1	$(\frac{1}{2}\frac{1}{2})$	$1/\sqrt{3}$	$-\sqrt{\frac{2}{3}}$
	7	$(\frac{3}{2}\frac{1}{2})$	$\sqrt{\frac{2}{3}}$	$1/\sqrt{3}$
600^+	0	(00)	$\frac{1}{2}$	$-\sqrt{3}/2$
	8	(11)	$\sqrt{3}/2$	$\frac{1}{2}$

For hydrogenic functions with $Z = 1$, if

$$|2s\rangle = (32\pi)^{-1/2}(2 - r)e^{-r/2}, \qquad (2.17\text{a})$$

then we must let

$$|2p_0\rangle = -(32\pi)^{-1/2}\, z e^{-r/2}. \qquad (2.17\text{b})$$

A generalized Runge-Lenz vector defined in this way is related to the hydrogenic vector by the same unitary transformation that transforms the $2s$ and $2p$ functions of Eqs. (2.16) into hydrogenic $2s$ and $2p$ functions.

III. HAMILTONIAN OF PROBLEM AND ITS MATRIX REPRESENTATION FOR STATES IN $2s$-$2p$ SHELL

We shall first consider that our system of electrons in the $2s$-$2p$ shell has a Hamiltonian of the form

$$H = \sum_{i=1}^{n}\left(\frac{1}{2m}p_i^2 - \frac{Z'e^2}{r_i}\right) + \sum_{i<j=1}^{n} V(r_{ij}) = H_0 + \mathcal{V}\ . \qquad (3.1)$$

As this Hamiltonian is acting within the shell, we may consider it as an effective rather than the actual Hamiltonian. Thus we have designated the charge of the nucleus by Z' rather than by the full Z of the atom in question, to stress that it may be an effective rather than actual charge. We furthermore represent the interaction by an, as yet, undetermined central interaction $V(r_{ij})$, rather than by the e^2/r_{ij} associated with the Coulomb repulsion.

We shall assume in this section that our single-particle states are those of a Coulomb potential of charge Z'. Thus in the matrix elements of H with respect to states with definite number of electrons n, the single-particle part contributes a constant and we need only concern ourselves with the evaluation of the matrix element

$$\tfrac{1}{2}n(n-1)\langle n\,S\,L\,\pi\,d'\,|V(r_{12})|\,n\,S\,L\,\pi\,d\rangle \qquad (3.2\text{a})$$

or, equivalently,

$$\tfrac{1}{2}n(n-1)\langle n\,S\,L\,\pi(\mu\nu)'\,|\,V(r_{12})\,|\,n\,S\,L\,\pi(\mu\nu)\rangle, \qquad (3.2\text{b})$$

which are diagonal in S, L, and π, as $V(r_{12})$ is a central force.

In Appendix B we discuss fully the evaluation of the matrix elements (3.2) by noting that the operator corresponding to $\sum V(r_{ij})$ in the second-quantized picture can be expressed as a sum of operators that are diagonal for states either in the $U(4) \supset O(4)$ chain, or in the $U(4) \supset U(3)$ chain, or in both. Furthermore, the diagonal matrix elements of these operators can be immediately evaluated, as they are all essentially Casimir operators of groups in the chain (2.14), (2.15). Introducing the abbreviated notation for the Slater integrals,[6] we obtain in (B8) of Appendix B the explicit form of the two-body interaction within the L shell. For the case in which d is either 0 or 2, it is easy to see that the Casimir operator $\mathcal{G}$ of $U(3)$ can be expressed in the form

$$\mathcal{G} = 5(\mathcal{N} - \mathcal{D}) - \tfrac{1}{2}(\mathcal{N} - \mathcal{D})^2 - 2\mathcal{S}^2. \qquad (3.3)$$

It follows then for the states in the even complexes of Tables II or III, the interaction operator takes the form

$$\begin{aligned}\mathcal{V} = {} & \tfrac{1}{2}F^0(2s,\ 2s)\,\mathcal{D}(\mathcal{D}-1) + F^0(2s,\ 2p)\,\mathcal{D}(\mathcal{N}-\mathcal{D}) \\ & + \tfrac{1}{6}G^1(2s,\ 2p)\,(\mathcal{A}^2 - \mathcal{N} - 2\mathcal{D}) \\ & + \tfrac{1}{2}F^0(2p,\ 2p)\,(\mathcal{N}-\mathcal{D})(\mathcal{N}-\mathcal{D}-1) \\ & + \tfrac{1}{25}F^2(2p,\ 2p)\,[10(\mathcal{N}-\mathcal{D}) - \tfrac{5}{2}(\mathcal{N}-\mathcal{D})^2 - \tfrac{3}{2}\mathcal{L}^2 - 6S^2].\end{aligned} \qquad (3.4)$$

Thus the two-body interaction appears as a linear combination of operators that are diagonal in the $U(3)$ basis only: $\mathcal{D}$, $\mathcal{D}^2$, and $\mathcal{N}\mathcal{D}$; an operator that is diagonal in $O(4)$ only: $\mathcal{A}^2$; and operators that are diagonal in each basis: $\mathcal{N}$, $\mathcal{N}^2$, $\mathcal{L}^2$, and $\mathcal{S}^2$. Denoting them, respectively, by $\mathcal{V}_u$, $\mathcal{V}_0$, $\mathcal{V}_{u0}$, we get

$$\mathcal{V} = \mathcal{V}_u + \mathcal{V}_0 + \mathcal{V}_{u0},$$

$$\begin{aligned}\mathcal{V}_u = {} & \tfrac{1}{2}F^0(2s,\,2s)\,\mathcal{D}(\mathcal{D}-1) + F^0(2s,\,2p)\,\mathcal{D}(\mathcal{N}-\mathcal{D}) \\ & - \tfrac{1}{3}G^1(2s,\,2p)\,\mathcal{D} + \tfrac{1}{2}F^0(2p,\,2p)\,\mathcal{D}(\mathcal{D}+1-2\mathcal{N}) \\ & - \tfrac{1}{10}F^2(2p,\,2p)\,\mathcal{D}(\mathcal{D}-2\mathcal{N}+4),\end{aligned}$$

$$\mathcal{V}_0 = \tfrac{1}{6}G^1(2s,\,2p)\,\mathcal{A}^2,$$

$$\mathcal{V}_{u0} = -\tfrac{1}{6}G^1(2s,\,2p)\mathcal{N} + \tfrac{1}{2}F^0(2p,\,2p)\,\mathcal{N}(\mathcal{N}-1)$$
$$-\tfrac{1}{50}F^2(2p,\,2p)\,[5\mathcal{N}(\mathcal{N}-4)+3\mathcal{L}^2+12\mathcal{S}^2]. \quad (3.5)$$

To evaluate the in-shell contribution to the energy of states of Table I, one of course simply inserts the appropriate eigenvalues into (3. 2).

To evaluate the contribution of the nondiagonal operators, one makes use of the transformation brackets of Table IV,

$$\langle n\,S\,L\,\pi\,d\,|\,n\,S\,L\,\pi(\mu\,\nu)\rangle \equiv \langle d\,|\,(\mu\nu)\,\rangle\,. \quad (3.6)$$

Thus

$$\langle d'\,|\,\mathcal{V}_0\,|\,d\,\rangle = \sum_{\mu\nu}\langle d'\,|\,(\mu\nu)\rangle\,\langle(\mu\nu)\,|\,\mathcal{V}_0\,|(\mu\nu)\,\rangle\,\langle(\mu\nu)\,|\,d\,\rangle\,,$$
$$(3.7)$$
$$\langle(\mu\nu)'\,|\,\mathcal{V}_u\,|\,(\mu\nu)\rangle = \langle(\mu\nu)'\,|\,2\rangle\,\langle 2\,|\,\mathcal{V}_u\,|\,2\rangle\,\langle 2\,|\,(\mu\nu)\rangle\,.$$

In the first case the sum contains two terms, but in the second only the term with $d=2$ contributes because $\mathcal{V}_u$ annihilates $U(3)$ states with $d=0$. In this manner one obtains the results of Tables II and III.

Tables I–IV provide us then with the fundamental results we need for any calculation of energies of atomic states between lithium and neon. However, we have not, as yet, included the contribution of the (1s) electrons in the closed-shell configuration.

IV. INCLUSION OF EFFECT OF 1s SHELL

The states we would like to consider now have, when classified by the $U(4)\supset U(3)$ chain, the configuration $(1s)^2\,(2s)^d\,(2p)^{n-d}$, where $n+2$ is now the total number of electrons. The corresponding kets

$$|\,(1s)^2(2s)^d(2p)^{n-d}\,S\,M_S\,L^\pi\,M_L\rangle \equiv |\,n\,S\,L^\pi d) \quad (4.1)$$

could still be denoted by the shorthand notation of the right-hand side, but we use the round bracket |) to distinguish them from the states (2. 1) with angular bracket | ⟩, where the 1s shell was not included.

The Hamiltonian of our problem now has the form

$$H = \sum_{i=1}^{n+2}\left(\frac{1}{2m}\,p_i^2 + U(r_i)\right) + \sum_{i<j=2}^{n+2} V(r_{ij})\,, \quad (4.2)$$

where for both the common and interacting potentials we assume, as yet, undertermined expressions.

The inclusion of a closed shell in the analysis has been discussed both by Condon and Shortley[6] and by de-Shalit and Talmi.[7] The matrix elements of H with respect to the states (4. 1) are given by

$$2I(1s)+d\,I(2s)+(n-d)\,I(2p)$$
$$+F^0(1s,\,1s)+2dF^0(1s,\,2s)+2(n-d)\,F^0(1s,\,2p)$$
$$-d\,G^0(1s,\,2s)-\tfrac{1}{3}(n-d)\,G^1(1s,\,2p)$$
$$+(\text{matrix elements in Tables I or II}). \quad (4.3)$$

Had we chosen to characterize the states by the $U(4)\supset O(4)$ rather than by the $U(4)\supset U(3)$ chain, the 1×1 matrices for which n, S, L, and π completely characterize the states remain unchanged, but the 2×2 matrix elements have to be obtained by carrying out a similarity transformation on (4. 3) using the 2×2 orthogonal matrices of Table IV. This has already been done in Table III for the last matrix elements in (4. 3), so we need only to carry out the transformation for the part that is associated with the interaction of the (1s) with the (2s-2p) shells. We thus obtain the matrix elements of the Hamiltonian (4. 2) with respect to the states (4. 1), or the corresponding states where ($\mu\nu$) replaces d.

V. ESTIMATION OF SYMMETRY BREAKING AND CONFIGURATION MIXING

The fundamental criterion that a perfect quantization scheme must satisfy is that it diagonalize the interaction of interest.

For a matrix

$$\begin{pmatrix} E_a & V_{ab} \\ V_{ab} & E_b \end{pmatrix}$$

with eigenvalues

$$E_\pm = \tfrac{1}{2}\{E_a + E_b \pm [(E_a - E_b)^2 + 4V_{ab}]^{1/2}\}$$

and corresponding eigenvectors $(C_{a\pm},\,C_{b\pm})$, we may measure the deviation from a diagonal matrix in several ways. Define parameters

$$\Delta \equiv E_a - E_b \quad \text{and} \quad \delta \equiv V_{ab}/\Delta\,.$$

A convenient criterion of the energy effect of the off-diagonal elements is then given by

$$|E_a - E_+|\,/\,|\Delta| = |\tfrac{1}{2}[1-(1+4\delta^2)^{1/2}]| \equiv |\epsilon|\,.$$

One measure of the effect of V_{ab} on the eigenvectors is given by the deviation of the ratio $|C_{b+}/C_{a+}|$ from zero. We have

$$\lambda \equiv |C_{b+}/C_{a+}| = |\epsilon|\,/\,|\delta|\,.$$

Another natural measure is supplied by the overlap between the vector $(C_{a+},\,C_{b+})$, say, and the vector (1, 0), which we measure by the *square* of their scalar product. Table V lists a few representative values of $\epsilon(\delta)$, $\lambda(\delta)$, and this overlap.

Using the analysis of the previous sections, let us now determine the extent to which the two $O(4)$ or $U(3)$ configurations of a complex interact. The $1/Z$ expansion allows us to begin with hydrogenic systems and consider their transformation into Hartree-Fock and extended Hartree-Fock systems. One writes

$$H' \equiv \frac{H}{Z^2} = \sum_i\left(\tfrac{1}{2}\pi_i^2 - \frac{1}{\rho_i}\right) + \frac{1}{Z}\sum_{i<j}\frac{1}{\rho_{ij}}\,, \quad (5.1)$$

where

$$\vec{\rho}_i \equiv Z\,\vec{r}_i\,, \quad \vec{\pi}_i \equiv -(-1)^{1/2}\frac{\partial}{\partial\vec{\rho}_i}\,; \quad \rho_i = |\vec{\rho}_i|\,,\ \text{etc.}$$

TABLE V. Relation between measures of symmetry breaking.

δ	$\lvert\epsilon\rvert$ (%)	λ	Overlap
0.05	0.3	0.05	0.998
0.10	1	0.09	0.990
0.25	6	0.24	0.949
0.50	21	0.41	0.854
1.00	62	0.62	0.724

and one then considers the final term as a perturbation which, at first, operates within the manifold of hydrogenic configurations. In terms of operators of the groups $O(4)$ and $U(3)$

$$H' = -\tfrac{1}{2}\textstyle\sum_i (A_i^2 + L_i^2 + 1)^{-1} + (1/Z)\,V \equiv H_0 + (1/Z)\,V, \qquad (5.2)$$

where V is the operator of Eqs. (3.4) and (4.3). It is to be understood that $\vec{A}_i$ is constructed from the dynamical variables $\vec{\rho}_i$ and $\vec{\pi}_i$, while in V, $\vec{A} = \sum \vec{A}_i$, $\vec{L} = \sum \vec{L}_i$, and $\vec{S} = \sum \vec{S}_i$.

The degeneracy in each hydrogenic complex needs first to be removed, and it has become evident that this is an important point in ordinary Hartree-Fock calculations where systematic discrepancies exist between single-configuration calculations and extended, two-configuration calculations that are relatable to just this degeneracy.[3,8] We shall begin by considering the contribution to the first-order configuration mixing that is due to interactions within the L shell at large Z, and then let Z approach n. Later, we will allow Z to increase by 2, and put two electrons in the K shell in order to consider the consequences of the interaction with the real core.

From Eq. (3.4) we can immediately obtain the conditions that would preserve $O(4)$ or $U(3)$ quantization within the shell. The portion of the operator (3.4) that is not diagonal in $O(4)$ is

$$\begin{aligned}\mathcal{V}_u = \{&-\tfrac{1}{2}F^0(2s,2s) + \tfrac{1}{2}F^0(2p,2p) - \tfrac{1}{3}G^1(2s,2p)\\ &- \tfrac{2}{5}F^2(2p,2p)\}\mathfrak{D}\\ &+ \{\tfrac{1}{2}F^0(2s,2s) + \tfrac{1}{2}F^0(2p,2p) - F^0(2s,2p)\\ &- \tfrac{1}{10}F^0(2p,2p)\}\,\mathfrak{D}^2\\ &+ \{F^0(2s,2p) - F^0(2p,2p) + \tfrac{1}{5}F^2(2p,2p)\}\mathfrak{N}\mathfrak{D}\cdot\end{aligned} \qquad (5.3)$$

The portion that is diagonal and that has different eigenvalues for different $O(4)$ members of the same complex is

$$\mathcal{V}_0 = \tfrac{1}{6}G^1(2s,2p)\,\alpha^2. \qquad (5.4)$$

If there were no interaction $\mathcal{V}_0$, the eigenstates of H' would be eigenstates of $\mathcal{V}_u$ also. Now because

$$\mathcal{V}_u|d\rangle = 0 \quad \text{if} \quad d = 0, \qquad (5.5)$$

it follows that in the presence of $\mathcal{V}_0$ and $\mathcal{V}_{u0}$ [Eq. (3.5)], $\mathcal{V}_u$ determines the energy of a $U(3)$ configuration, $\mathcal{E}_d$, with respect to the configuration with no $2s$ electrons. It follows that

$$\begin{aligned}\langle(\mu\nu)'|\mathcal{V}_u|(\mu\nu)\rangle &= \langle(\mu\nu)'|2\rangle\langle 2|\mathcal{V}_u|2\rangle\langle 2|(\mu\nu)\rangle\\ &= \langle(\mu\nu)'|2\rangle(\mathcal{E}_2 - \mathcal{E}_0)\langle 2|(\mu\nu)\rangle,\end{aligned} \qquad (5.6)$$

where the right-hand side of (5.6) is a consequence of the definition

$$\mathcal{E}_d = \langle d|H_0 + \mathcal{V}_{0u} + \mathcal{V}_u|d\rangle . \qquad (5.7)$$

The $O(4)$ basis therefore diagonalizes the Hamiltonian if and only if the two $U(3)$ configurations are initially degenerate, that is, degenerate in the absence of v_0. On the other hand, $U(3)$ cannot be a perfect symmetry unless the exchange integral $G^1(2s, 2p)$ vanishes. This is because in the expression for the $U(3)$ off-diagonal elements

$$\begin{aligned}\langle d'|\mathcal{V}_0|d\rangle &= \sum_{\mu\nu}\langle d'|(\mu\nu)\rangle\langle(\mu\nu)|\mathcal{V}_0|\mu\nu)\rangle\langle(\mu\nu)|d\rangle\\ &= \tfrac{1}{6}G^1(2s,2p)\sum_{\mu\nu}\langle d'|(\mu\nu)\rangle\,2[\mu(\mu+1) + \nu(\nu+1) - l(l+1)]\langle(\mu\nu)|d\rangle\end{aligned} \qquad (5.8)$$

the sum never vanishes, as can be seen from Table IV.

For hydrogenic functions the Slater integrals have the following values:

$$F^0(2s,2s) = \frac{Z'e^2}{a_0}\,\frac{77}{512}, \qquad F^0(2p,2p) = \frac{Z'e^2}{a_0}\,\frac{93}{512},$$

$$G^1(2s,2p) = \frac{Z'e^2}{a_0}\,\frac{45}{512},$$

$$F^0(2s,2p) = \frac{Z'e^2}{a_0}\,\frac{83}{512}, \qquad F^2(2p,2p) = \frac{Z'e^2}{a_0}\,\frac{45}{512}.$$

Inserting these in (5.3), we obtain

$$\mathcal{V}_u = -\frac{Z'e^2}{a_0}\,\frac{1}{5120}\{250\mathfrak{D} + 25\mathfrak{D}^2 + 10\mathfrak{N}\mathfrak{D}\}. \qquad (5.9)$$

Similarly, (5.4) yields

$$\mathcal{V}_0 = \frac{Z'e^2}{a_0}\,\frac{75}{5120}\,\alpha^2 . \qquad (5.10)$$

From Table IV we find then that the contribution of (5.3) to the $O(4)$ off-diagonal elements is

$$\langle(\mu\nu)'|\mathcal{V}_u|(\mu\nu)\rangle = \langle(\mu\nu)'|2\rangle\langle 2|(\mu\nu)\rangle\left(\frac{-Z'e^2}{a_0}\right)\frac{600 + 20n}{5120}, \qquad (5.11)$$

TABLE VI. $U(3)$ and $O(4)$ overlaps of eigenkets of L-shell interaction for hydrogenic functions.

Complex	$U(3)$ overlap Lowest state	$O(4)$ overlap Lowest state
200	0.76	0.72
$3\frac{1}{2}1$	0.88	0.67
400	0.87	0.83
402	0.96	0.70
411	0.96	0.70
$5\frac{1}{2}1$	0.95	0.86
600	0.95	0.92

while its contribution to the difference between the diagonal elements is

$$[\,|\langle(\mu\nu)|2\rangle|^2 - |\langle(\mu\nu)'|2\rangle|^2\,]\left(\frac{-Z'e^2}{a_0}\right)\frac{600+20n}{5120}\ . \tag{5.12}$$

In Tables II and III we have given the total matrix elements of the operators (3.3) for kets composed of hydrogenic functions. Diagonalizing these matrices using (5.11) and (5.12), one obtains the eigenvectors of each complex. In Table VI we display the overlap of the lowest-energy eigenvector of each pair with the corresponding $O(4)$ and $U(3)$ eigenvectors. It is evident from the table that while the interaction acts to break both $U(3)$ and $O(4)$ symmetry, $U(3)$ quantum numbers retain more validity than their $O(4)$ counterparts in this basis set. It is also evident that, from $n=3$ on, there is a general tendency for $O(4)$ quantization to improve as the number of electrons increases.

Consider now the effect of continuously increasing the parameter $1/Z$ from an infinitesimal value to the value $\frac{1}{10}$ to $\frac{1}{3}$ that is appropriate for second-row atoms. The complete solution of the extended Hartree-Fock problem for each value of the parameter $1/Z$ will produce values for each of the F, G integrals. It has been apparent for some time that the Z dependence of these values is a very nearly linear one for a wide range of atoms and ions in their ground and excited states. From the recent tabulation of Condon and Odabasi,[9] one finds that for $6 \leqslant Z \leqslant 20$ the integrals for ordinary configurations obey the following relation remarkably well:

$$R^k_{ab}(Z) = (Z - s^{kc}_{ab})R^k_{ab}(H)\,, \quad R^k = F^k,\ G^k \tag{5.13}$$

where $R(H)$ is the value of R obtained using hydrogenic functions with $Z=1$, and the screening parameters s^{kc}_{ab} depend upon the configuration c as well as the orbitals a and b. In Table VII we have calculated average values of the parameters s by inverting (5.13) and inserting the tabulated values of Z, $R^k_{ab}(Z)$, and the hydrogenic integral. Deviations from (5.13) become appreciable for $Z<6$, so the screening parameters have been calculated using Z values greater than 5.

It is apparent that even for values $1/Z<\frac{1}{20}$ there has been a pronounced shift of the Hartree-Fock values below the hydrogenic values. The screening parameters should therefore be dealt with in the first-order terms of the $1/Z$ expansion, using screened hydrogenic functions as Layzer has emphasized.[3]

With a screening parameter ξ^c, common to all orbitals, we may then write

$$E^c = T_1(Z-\xi^c)^2 + V_1 Z(Z-\xi^c) + \epsilon_1(Z-\xi^c)\,, \tag{5.14}$$

where T_1, V_1, and ϵ_1 are, respectively, the kinetic energy, nuclear electronic potential energy, and electronic repulsion energy when hydrogenic orbitals with $Z=1$ are used to build the configuration c. Choosing ξ^c variationally and making use of the virial relation $2T_1 = -V_1$, one finds

TABLE VII. Z dependence of Hartree-Fock Slater integrals (Ref. 9).

					Difference of integrals for $Z+1$ and Z		
n	Config.	Integral	s_{av}	$R(H)$	$Z=n$	$Z=n+5$	$Z=n+10$
4	$1s^22s^2$	F^0_{2s2s}	1.503 56	0.300 78	0.324 08	0.303 49	0.301 71
	$1s^22p^2$	F^0_{2p2p}	2.132 98	0.363 28	0.386 32	0.386 18	0.365 11
		F^2_{2p2p}	2.301 32	0.175 78	0.185 29	0.177 76	0.176 61
	$1s^22s2p$	F^0_{2s2p}	1.749 62	0.324 22	0.362 68	0.328 42	0.325 76
		G^1_{2s2p}	1.110 02	0.175 78	0.231 13	0.181 08	0.177 64
6	$1s^22s^22p^2$	F^0_{2s2s}	2.014 12	0.300 78	0.297 15	0.302 14	0.301 45
		F^0_{2s2p}	2.294 72	0.324 22	0.354 29	0.328 70	0.326 03
		G^1_{2s2p}	1.549 31	0.175 78	0.218 17	0.182 23	0.178 35
		F^0_{2p2p}	2.714 73	0.363 28	0.413 15	0.370 29	0.366 10
		F^2_{2p2p}	2.964 40	0.175 78	0.202 04	0.179 37	0.177 22
8	$1s^22s^22p^4$	F^0_{2s2s}	2.573 55	0.300 78	0.290 35	0.301 08	0.301 13
		F^0_{2s2p}	2.928 40	0.324 22	0.343 04	0.328 39	0.326 08
		G^1_{2s2p}	2.050 53	0.175 78	0.208 76	0.183 47	0.179 21
		F^0_{2p2p}	3.455 37	0.363 28	0.401 25	0.370 45	0.366 41
		F^2_{2p2p}	3.810 74	0.175 78	0.196 53	0.179 63	0.177 44

$$\xi^c = |\epsilon_1/V_1| . \tag{5.15}$$

Note that ξ is independent of the nuclear charge Z and so is appropriate to finite values of the expansion parameter $1/Z$. It is evidently necessary also to improve this approximation in first order by minimizing the energy with respect to individual orbital screening parameters

$$\xi^c_{aa} = \xi^c + \tau^c_{aa} ,$$

while taking into account the necessity of orthogonalizing the resulting radial wave functions. Thereafter, as Layzer[3] has shown from an analysis of the experimental data, the first-order $1/Z$ expansion gives results that are much better than those of the usual theory dealt with in Condon and Shortley.

If one chooses ξ^c according to the relation (5.15) for the lower states of our L-shell complexes, and then minimizes their energy with respect to ξ^c_{2s} and ξ^c_{2p}, one finds that the energy is changed only very slightly and that $\xi^c_{2s} \approx \xi^c_{2p} \approx \xi^c$. Thus in the series with two electrons in the L shell we have $\xi^c_{2p} - \xi^c_{2s} < 0.02$, and the energy lowering when $Z = 2$ is less than $0.0001 e^2/a_0$ or 0.004% of the difference in energy between the upper and lower state, while in the series with six electrons in the L shell we have $\xi^c_{2p} - \xi^c_{2s} < 0.2$, and the improvement in the energy when $Z = 6$ is $0.014 e^2/a_0$ or 4% of the difference in energy between the upper and lower state.

In short, as one expects, in the L shell, intrashell shielding effects are of minor importance when there is no K shell. Consequently, as $Z \rightarrow n$, all the L-shell electron repulsions should remain proportional to $Z - s$. If complete Hartree-Fock calculations were done on these neutral atoms lacking K shells, treating them as doubly excited states of neutral atoms, the matrix elements of $\mathcal{V}_0$ and $\mathcal{V}_u$ would each be proportional to $Z - s$. Consequently we expect to find the same configuration-mixing parameters when $Z = n$ that one finds as $Z \rightarrow \infty$.

Let us now deal with the effects of the interaction between the L shell and the core when the interaction is no longer simply a Coulombic attraction to the nucleus, but is the interaction with the nucleus and the K-shell electrons. For this purpose we replace the operator (3.4) by the operator of (4.3) and suppose that in the neutral atoms the nuclear charge is increased by 2, as the K shell is doubly occupied. The differences in symmetry breaking that we find are then due to the difference between a purely Coulombic interaction of the L electrons with the nucleus and the shielded interaction due to the presence of the K electrons. The additional operator involved is diagonal in $U(3)$ but not in $O(4)$. As is well known, it separates the energies of the configurations $1s^2 2s^2 2p^x$ and $1s^2 2p^{x+2}$ by amounts in excess of e^2/a_0. [An algebraic estimate of the effect of the core interactions in breaking $O(4)$ symmetry has been given by Perelomov, Popov, and Terentev.[10]] If we allow it to act on hydrogenic complexes that are also interacting among themselves via the operator (3.4), we get the zero-order results of the Z-expansion approximation to the extended Hartree-Fock theory of normal atoms.[8, 11] The overlap of the resulting functions with $O(4)$ and $U(3)$ IR is given in Table VIII.

We may improve these functions somewhat if we include in them a common nuclear charge parameter Z' and minimize the energy with respect to it. The overlap of the resulting eigenfunctions with $O(4)$ and $U(3)$ functions is displayed in Table IX. As one would expect, the $U(3)$ classification retains a large measure of validity for both sets of calculations, while $O(4)$ does not.

Clementi and Veillard[12] and McKoy and Sinanoğlu[8] have carried out extensive SCF calculations on first-row atoms and have allowed for the interactions between configurations of a number of complexes. In Table X we indicate the extent to which the Clementi-Veillard wave functions overlap $O(4)$ and $U(3)$ functions. It is apparent that in all cases the complete interaction again favors $U(3)$ symmetry. In Table X we also compare the Clementi-Veillard mixed configurations with the hydrogenic ones that are appropriate as $Z \rightarrow \infty$. The effect of moving from infinitesimal $1/Z$ to finite $1/Z$ is seen to be extremely small, even in the case of Be, where $1/Z = \frac{1}{4}$.

Sinanoğlu and Alper have concluded that, in B and C, $O(4)$ symmetry is preserved by the L-shell interactions between Hartree-Fock functions that have been calculated for atoms with complete K shells.[13] We examine this point in Tables XI and XII. In neutral atoms it is apparent that for this interaction $O(4)$ is a much better symmetry than $U(3)$. However, this does not remain true as one successively removes electrons from oxygen to obtain members of the N, C, and B series with successively higher nuclear charges.

In Table XIII we have analyzed the contributions to the $O(4)$ off-diagonal elements in the neutral

TABLE VIII. $U(3)$ and $O(4)$ overlaps of eigenkets of K- and L-shell interactions for hydrogenic functions with $Z' = 1$.[a]

Complex	Atom	$U(3)$ overlap Lowest state	$O(4)$ overlap Lowest state
200	Be	0.949	0.465
$3\frac{1}{2}1$	B	0.972	0.496
400	C	0.960	0.697
402	C	0.989	0.605
411	C	0.988	0.605
$5\frac{1}{2}1$	N	0.982	0.783
600	O	0.980	0.863

[a] Calculated from eigenvectors of Ref. 10.

TABLE IX. $U(3)$ and $O(4)$ overlaps of hydrogenic functions with energy-optimized scale parameter.

Atom and multiplet	Z' optimal	Minimized energies (a.u.)	Experimental energies (a.u.)	Overlap $U(3)$ state with $d=2$	(%) $O(4)$ state with A^2+L^2 minimum.
Be $^1S^+$	3.376	−14.2	−14.669	94	48.5
		−13.504	−14.343	6	51.5
B $^2P^-$	4.159	−23.8	−24.659	97	50.5
		−22.65		3	49.5
C $^1S^+$	4.899	−36.0	−37.758	95.5	71.
		−34.6		45	29
C $^1D^+$	4.907	−36.16	−37.810	99	60
		−34.8		1	40
C $^3P^+$	4.914	−36.33	−37.856	99	60
		−34.9		1	40
N $^2P^-$	5.646	−51.9	−54.482	98.5	77.5
		−50		1.5	22.5
O $^1S^+$	6.369	−71.0	−74.958	98	86
		−68.7		2	14

atoms. We see that, unlike the situation with hydrogenic functions, the sign of the $\mathfrak{MD}$ contribution is opposite to that of the $\mathfrak{D}$ and $\mathfrak{D}^2$ contributions. As n increases, we reach, in the neutral carbon atom, a point where the two contributions very nearly cancel and each pair of $U(3)$ configurations in each complex is almost degenerate when the core and $\mathfrak{A}^2$ interactions are disregarded. In several other cases in Table XI, where $U(3)$ is a particularly poor symmetry group though $O(4)$ is not outstandingly good, the $U(3)$ configurations of a complex are nearly degenerate because of additional contributions from the $\mathfrak{A}^2$ interaction.

For a given value of n, as Z increases, the contribution of each of the Slater integrals changes, but now, because the effective nuclear charges are not all the same, the configuration mixing is not stable, and we do not find that $O(4)$ continues to be a good symmetry group for the interaction.

VI. CONCLUSIONS

It is apparent that analysis of operators and wave functions into $O(4)$ and $U(3)$ components provides a greatly simplified way of dealing with calculations on first-row atoms. A result that emerges from the analysis is the full extent of the stability of L-shell configuration mixing to variations in Z from values near n to values approaching infinity. The near invariance of this mixing is found to hold in normal first-row atoms and ions, in their excited states, and in states having two holes in the K shell. Tuan and Sinanoğlu some time ago called attention to the weak dependence of $^1S(2s^2)$-$^1S(2p^2)$ mixing upon the form of the radial functions.[14] The Z stability of mixing in ground states has been evident from the aforementioned study of Layzer,[3] while a comparison of the work of Cohen and Dalgarno[15] on transition probabilities with that[16] of Iutsis and Kovetshis, Bolotin and Iutsis, and Bolotin *et al.*, shows that for several individual systems the stability holds for excited states as well. A fully group-theoretical understanding of these near-invariances awaits an analysis in terms of the dynamical noninvariance groups of Coulomb systems.[17] It must not be supposed, however, that this Z independence is universal: Configuration mixing in the third shell can be markedly Z dependent, as has been emphasized by Fischer.[18]

Finally, we wish to call attention to the fact that the first entry in Table VII is in contradiction with the earlier results of Wulfman.[19] The latter are in error because of an incorrect assessment of the phase convention used by Lipsky and Russek in their calculations on helium doubly excited states.[20] We wish to thank Wybourne for an intensive correspondence that enabled us to clear up this point. It is now evident that neither $O(4)$ nor $U(3)$ provides a good quantization scheme for L-shell

TABLE X. Overlaps with unrestricted Hartree-Fock functions.[a]

Complex	Atom	$U(3)$ overlap lowest state	$O(4)$ overlap lowest state	Overlap with zero-order function
200	Be	0.839	0.561	0.991
$3\frac{1}{2}1$	B	0.947	0.564	0.995
411	C	0.978	0.648	0.998
$5\frac{1}{2}1$	N	0.968	0.823	0.998
600	O	0.962	0.897	0.997

[a] Calculated from eigenvectors of Ref. 12.

TABLE XI. In-shell off-diagonal matrix elements in Hartree-Fock approximation.[a]

States *nSL*	Atom	In-shell contribution $O(4)$	In-shell contribution $U(3)$	Δ[b] $O(4)$	δ[b] $O(4)$	δ[b] $U(3)$	Δ[b] $U(3)$
200	Be	−0.0616	−0.1129	−0.1897	0.3247	−9.5678	0.0118
$3\frac{1}{2}1$	B	−0.0330	−0.0859	−0.1589	0.2077	−9.2366	0.0093
	O^{+3}[c]	−0.238	−0.182	−0.218	1.096	−0.483	0.377
400	C	−0.0176	−0.2292	−0.4583	0.0384	−6.5114	0.0352
402	C	−0.0176	−0.1146	−0.2292	+0.0768	−3.2557	0.0352
411	C	−0.0176	+0.1146	+0.2292	−0.0768	+3.2557	0.0352
400	O^{+2}[d]	−0.187	−0.365	−0.731	0.256	−0.976	0.374
402	O^{+2}[d]	−0.187	−0.183	−0.365	0.512	−0.488	0.374
411	O^{+2}[d]	−0.187	+0.183	+0.365	−0.512	+0.488	0.374
$5\frac{1}{2}1$	N	−0.0799	0.1895	−0.3455	0.2313	−5.3230	−0.0356
$5\frac{1}{2}1$	O^{+}[c]	0.0598	0.2433	−0.5585	−0.1071	0.8140	0.2989
600	O	−0.1659	0.2685	−0.4283	0.3874	−3.6630	−0.0733

[a] Parameters for neutral atoms were computed from integrals of Table XII.

[b] For definition of Δ, δ see Sec. V.

[c] Parameters for O^{+} were computed from the integrals of A. J. Freeman, quoted in J. C. Slater's, *Quantum Theory of Atomic Structure*, Vol. I. p. 357–8 (McGraw-Hill, New York, 1960).

[d] Parameters for O^{+2} and O^{+3} are from D. R. Hartree. W. Hartree, and B. Swirles, Phil. Trans. Roy. Soc. London A238, 229 (1939).

systems containing no K electrons.

APPENDIX A: CLASSIFICATION AND DETERMINATION OF STATES IN 2*s*-2*p* SHELL

When dealing with a system of particles obeying Fermi statistics that are restricted to a finite number of single-particle configurations, it is always convenient to use the second-quantization formalism.[5]

In the $2s$-$2p$ shell the single-particle states could be characterized by the set of quantum numbers

$$2lm\sigma \quad \text{or} \quad (\tfrac{1}{2}\tfrac{1}{2})lm\sigma\,, \tag{A1}$$

where $l=0$, 1 stands for the orbital angular momentum in the $2s$ or $2p$ subshell, respectively, m is the projection of l, and $\sigma=\pm\frac{1}{2}$ is the projection of the spin. The number 2 indicates the total quantum number in the shell and $(\frac{1}{2}\frac{1}{2})$ the equivalent IR of $O(4)$, as discussed in Sec. II.

As the numbers 2 or $(\frac{1}{2}\frac{1}{2})$ will remain fixed so long as we stay within the $2s$-$2p$ shell, we suppress them from the indices of the anticommuting creation and annihilation operators, which we write as

$$b^{\dagger}_{lm\sigma},\, b^{l'm'\sigma'} \quad . \tag{A2}$$

An arbitrary state of n particles is then given in terms of an homogeneous polynomial of degree n in the $b^{\dagger}$'s acting on the vacuum state $|0\rangle$.

The operators

$$\mathfrak{C}^{\alpha'}_{\alpha} \equiv \mathfrak{C}^{l'm'\sigma'}_{lm\sigma} = b^{\dagger}_{lm\sigma}\, b^{l'm'\sigma'}\,, \tag{A3}$$

where α is a shorthand notation for $lm\sigma$, satisfy the commutation relations

$$[\mathfrak{C}^{\alpha'}_{\alpha},\, \mathfrak{C}^{\beta'}_{\beta}] = \mathfrak{C}^{\beta'}_{\alpha}\,\delta^{\alpha'}_{\beta} - \mathfrak{C}^{\alpha'}_{\beta}\,\delta^{\beta'}_{\alpha}\,, \tag{A4}$$

which indicate that they are associated with a Lie

TABLE XII. Hartree-Fock parameters, in units of e^2/a_0.[a]

Atom	Configuration	F^0_{2s2s}	F^0_{2s2p}	F^0_{2p2p}	G^1_{2s2p}	F^2_{2p2p}
	$2s^2$	0.349 07				
Be	$2s2p$		0.322 53		0.195 57	
	$2p^2$			0.306 65		0.135 47
B	$2s^22p$	0.460 25	0.437 37		0.273 29	
	$2s2p^2$			0.417 73		0.189 76
C	^3P $2s^22p^2$	0.572 86	0.554 19	0.538 60	0.343 72	0.243 30
N	^2P $2s^22p^3$	0.688 79	0.657 66	0.631 67	0.401 98	0.280 66
O	^1S $2s^22p$	0.802 18	0.766 23	0.736 56	0.464 96	0.325 20

[a] Integrals are from S. Fraga and C. Fisk, University of Alberta Division of Theoretical Chemistry Technical Report No. TC 6801, 1968 (unpublished), except in the case of Be, where they are from Ref. 9.

algebra of an eight-dimentional unitary group $U(8)$ as

$$\begin{aligned}\alpha = lm\sigma, \quad &\text{with } l=1,\ m=1,\ 0-1,\ \sigma=\pm\tfrac{1}{2};\\ &l=0,\ m=0,\ \sigma=\pm\tfrac{1}{2}\ .\end{aligned} \tag{A5}$$

If we contract separately with respect to σ and lm, we obtain the operators

$$\mathfrak{C}_{lm}^{l'm'} = \sum_{\sigma} \mathfrak{C}_{lm\sigma}^{l'm'\sigma'}, \tag{A6a}$$

$$C_{\sigma}^{\sigma'} = \sum_{lm} \mathfrak{C}_{lm\sigma}^{lm\sigma'}\ , \tag{A6b}$$

which satisfy commutation relations similar to (A4) and thus, because of (A5), are, respectively, the generators of a $U(4)$ and a $U(2)$ group. The latter admits a unitary unimodular subgroup $SU^{\sigma}(2)$ whose generators

$$\mathcal{S}_{+} = C_{1/2}^{-1/2}, \quad \mathcal{S}_{0} = \tfrac{1}{2}(C_{1/2}^{1/2} - C_{-1/2}^{-1/2}), \quad \mathcal{S}_{-} = C_{-1/2}^{1/2} \tag{A7}$$

are the operators of total spin of the system.

The group $U(4)$ admits as a subgroup the unitary group in three dimensions $U(3)$, associated with the $2p$ shell whose generators are

$$\mathfrak{C}_{lm}^{lm'}, \quad m, m' = 1, 0, -1\ . \tag{A8}$$

Rather than discuss them in the form (A8), we replace them, as well as the full set of generators (A6a), by the unit tensor operators[21]

$$\mathfrak{U}_{q}^{k}(l, l') = \sum_{mm'} \langle l'km'q | lm \rangle \mathfrak{C}_{lm}^{l'm'}, \qquad l, l' = 0, 1,\ k = 0, 1, 2\ . \tag{A9}$$

The operators $\mathfrak{U}_{q}^{k}(1, 1)$ are then equivalent to the set of generators of $U(3)$ and, in particular,[5]

$$\sqrt{2}\,\mathfrak{U}_{q}^{1}(1, 1) \equiv \mathfrak{L}_{q}, \quad q = 1, 0, -1 \tag{A10}$$

are the generators of the proper orthogonal subgroup $O^{+}(3)$ of $U(3)$, i.e., the second-quantized form of the operators of total orbital angular momentum.

We have thus obtained the generators of all the groups associated with the chains (2.14), (2.15a). For the chain (2.15b) we need to have the second-quantized form of the Runge-Lenz vector, i.e.,[5,22]

$$\begin{aligned}\mathfrak{A}_{q} &= \sum_{lml'm'} \langle 2lm | A_{q} | 2l'm' \rangle \mathfrak{C}_{lm}^{l'm'}\\ &= \sum_{ll'} \langle 2l' || A || 2l \rangle \mathfrak{U}_{q}^{1}(l, l')\\ &= \mathfrak{U}_{q}^{1}(10) - \sqrt{3}\,\mathfrak{U}_{q}^{1}(01)\ .\end{aligned} \tag{A11}$$

Thus $\mathfrak{L}_{q}$ and $\mathfrak{A}_{q}$ are the generators of the $O(4)$ group.

To obtain now all quantum numbers for the states in the $2s$-$2p$ shell characterized by the IR of the chain of groups (2.14), (2.15), we proceed as follows: First, the number of particles n gives the IR $[1^{n}]$ of $U(8)$, and this indicates that the IR of $U(4)$ and $SU^{\sigma}(2)$ are given by associate[23] partitions of n. Thus the IR of $U(4)$ is characterized by a partition $f \equiv \{f_1 f_2 f_3 f_4\}$ of n, in which $f_1 \geq f_2 \geq f_3 \geq f_4 \geq 0$ and all $f_i \leq 2$, $i = 1, 2, 3, 4$. This Young diagram has then two columns whose total number of blocks is n, and half the difference between the first and second columns is the total spin S. Therefore n and S determine the partition f.

Once we have the IR f of $U(4)$, if we want to proceed by the chain $U(4) \supset U(3)$, we just remember the branching rule[24]

$$f_1 \geq h_1 \geq f_2 \geq h_2 \geq f_3 \geq h_3 \geq f_4 \geq 0 \tag{A12}$$

that gives us all possible IR of $U(3)$. The number of particles d in the $2s$ configuration is then obtained from

$$d = n - (h_1 + h_2 + h_3)\ . \tag{A13}$$

As the parity of the $2p$ state is negative and that of the $2s$ positive, the total parity of our state will be given by

$$(-)^{h_1 + h_2 + h_3} = (-)^{n-d}\ . \tag{A14}$$

Finally, to get the values of L in a given IR of $U(3)$, we use either the well-known[25] branching rule of $U(3) \supset O^{+}(3)$ or the familiar plethysm procedure.[26]

To get the values $(\mu\nu)$ of the IR of $O(4)$ in the IR f of $U(4)$, we again can use either the branching rule[27] $U(4) \supset O(4)$ or the plethysm procedure.[26] The values of L consistent with each $(\mu\nu)$ are given by (2.9). An important point in these analyses is to note that the vector $\vec{\mathfrak{L}}$ has positive parity, while $\vec{\mathfrak{A}}$ has negative parity. Thus the vectors $\vec{\mathfrak{M}}$ and $\vec{\mathfrak{N}}$ do not have definite parity and the states classified by the (2.15b) will likewise, in general, have no definite parity. We note though that under reflection $\vec{\mathfrak{M}}$ and $\vec{\mathfrak{N}}$ interchange their roles, and thus the combination of the states

TABLE XIII. Contributions to $O(4)$ symmetry-breaking interaction for Hartree-Fock functions.

Atom	n	ab^{a}	$\mathfrak{D}$ coeff.	$\mathfrak{D}^2$ coeff.	$\mathfrak{N}\mathfrak{D}$ coeff.	Total^{b}
Be	2	$\sqrt{3}/4$	−0.140 59	−0.008 21	+0.042 97	−0.142 14
B	3	$\sqrt{2}/3$	−0.188 26	−0.017 36	+0.057 59	−0.100 42
C	4	1/2	−0.229 02	−0.022 79	+0.064 25	−0.035 20
N	5	$-\sqrt{2}/3$	−0.274 81	−0.025 50	+0.082 12	+0.169 58
O	6	$-\sqrt{3}/4$	−0.317 88	−0.029 38	+0.094 71	+0.383 24

[a] $a = \langle \mu\nu | 2 \rangle$ $b = \langle (\mu\nu)' | 2 \rangle$.

[b] $2(\mathfrak{D}\text{ coeff.}) + 2^2(\mathfrak{D}^2\text{ coeff.}) + 2n(\mathfrak{N}\mathfrak{D}\text{ coeff.})$.

$$|nS(\mu\nu)L\rangle \pm (-)^{\mu+\nu-L}|nS(\nu\mu)L\rangle \tag{A15}$$

has even or odd parity depending on whether we use the + or − sign. The states (2.10) correspond to the combination (A15), and to avoid redundancy we choose always in Table I $\mu \geq \nu$.

We have thus indicated how we could classify the states in the $2s$-$2p$ shell. It remains to determine them explicitly, which we first do in the $U(4) \supset U(3)$ chain. We start by noting that what we require are the homogeneous polynomials P of degree n in the $b^\dagger$ that are associated with all the quantum numbers, i.e.,

$$|nSL^{\pi}d\rangle = P_{nSL^{\pi}d}(b^\dagger)|0\rangle \; . \tag{A16}$$

As we are not concerned with the values of M_L and M_S, we could choose them as $M_L = L$ and $M_S = S$, thus having to satisfy the equations

$$\mathcal{L}_0 P_{nSL^{\pi}d}(b^\dagger)|0\rangle = L P_{nSL^{\pi}d}(b^\dagger)|0\rangle \; , \tag{A17a}$$

$$\mathcal{L}_1 P_{nSL^{\pi}d}(b^\dagger)|0\rangle = 0 \; , \tag{A17b}$$

$$\mathcal{S}_0 P_{nSL^{\pi}d}(b^\dagger)|0\rangle = S P_{nSL^{\pi}d}(b^\dagger)|0\rangle \; , \tag{A18a}$$

$$\mathcal{S}_+ P_{nSL^{\pi}d}(b^\dagger)|0\rangle = 0 \; . \tag{A18b}$$

We could then take products of operators

$$b^\dagger_{l_1 m_1 \sigma_1} \cdots b^\dagger_{l_n m_n \sigma_n} \; , \tag{A19}$$

such that d of them have $l = 0$ and the rest $l = 1$, with the restrictions that

$$m_1 + \cdots + m_n = L \; , \quad \sigma_1 + \cdots + \sigma_n = S \; . \tag{A20}$$

Taking linear combination of all products of this type, with arbitrary coefficients, we determine the latter with the help of Eqs. (A17b) and (A18b). The procedure is unique, as there is only one state for each $nSL^{\pi}d$.

For the $U(4) \supset O(4)$ chain the states are the same when nSL^{π} characterize them completely. For the seven cases when we have two states with the same nSL^{π}, we first note that from (2.6) the operator $\mathfrak{A}^2$ is given by

$$\mathfrak{A}^2 = 2\mathfrak{M}^2 + 2\mathfrak{N}^2 - \mathcal{L}^2 \; ,$$

where $\mathfrak{M}$ and $\mathfrak{N}$ are the second-quantized versions of $\vec{\mathfrak{M}}$ and $\vec{\mathfrak{N}}$. Thus $\mathfrak{A}^2$ is diagonal for the states $|nSL^{\pi}(\mu\nu)\rangle$ with a definite eigenvalue. As we have obtained the states $|nSL^{\pi}d\rangle$, we can evaluate with respect to them the matrix of the $\mathfrak{A}^2$ operator and from its diagonalization determine the states $|nSL^{\pi}(\mu\nu)\rangle$. The 2×2 transformation matrices between the $U(4) \supset U(3)$ and $U(4) \supset O(4)$ states are given in Table II.

APPENDIX B

In the second-quantization formalism the expressions for a one-body $\sum_{i=1}^{n} W_i$ and a two-body $\sum_{i>j=1}^{n} V_{ij}$ spin-independent interaction are[5]

$$\mathcal{W} = \sum_{lml'm'} \langle lm|\, W_1 |\, l'm'\rangle \mathcal{C}_{lm}^{l'm'} \; , \tag{B1}$$

$$\mathcal{V} = \tfrac{1}{2} \sum_{l_1 l_2 m_1 m_2} \sum_{l'_1 l'_2 m'_1 m'_2} \langle l_1 m_1, l_2 m_2 |\, V_{12} |\, l'_1 m'_1, l'_2 m'_2 \rangle \left(\mathcal{C}_{l_1 m_1}^{l'_1 m'_1} \mathcal{C}_{l_2 m_2}^{l'_2 m'_2} - \delta_{l_2}^{l'_1} \delta_{m_2}^{m'_1} \mathcal{C}_{l_1 m_1}^{l'_2 m'_2} \right) \; , \tag{B2}$$

where the $\mathcal{C}_{lm}^{l'm'}$ are the generators of the $U(4)$ group acting on the configuration space of the $2s$-$2p$ shell and which were defined in Appendix A, Eq. (A6a), in terms of the creation and annihilation fermion operators. In the two formulas above the l's take the values 0 or 1.

In the case of a central one-body interaction, the matrix element in (B1) is diagonal in l and m and independent of m; hence $\mathcal{W}$ is expressed as a linear combination of the number operators for the $2s$ and $2p$ shells:

$$\mathcal{C}_{00}^{00} = \mathfrak{U}_0^0(00) \equiv \mathfrak{D}, \; \sum_{m=1}^{-1} \mathcal{C}_{1m}^{1m} = \mathfrak{U}_0^0(1,\, 1) \; . \tag{B3}$$

The coefficients of this linear combination are the one-electron Slater integrals

$$I(nl) = \int R_{nl}(r)\, W_1 R_{nl}(r)\, r^2 dr \; ,$$

where $R_{nl}(r)$ is the radial part of a wave function belonging to our basis. These operators (B3) are diagonal in the $U(3)$ basis, and their eigenvalues were denoted in the text by d and $n-d$, respectively. Obviously the total number operator is $\mathfrak{N} = \mathfrak{D} + \mathfrak{U}_0^0(1,\, 1)$.

Now, for the two-body central interaction we make an expansion

$$V_{12}(|\vec{r}_1 - \vec{r}_2|) = \sum_{k=0}^{\infty} V_k(r_1,\, r_2) P_k(\cos\omega_{12}) \; ,$$

and using a standard technique,[6] we write the two-particle matrix element in (B2) as

$$\langle l_1 m_1, l_2 m_2 |\, V_{12} |\, l'_1 m'_1, l'_2 m'_2 \rangle = \left(\frac{(2l'_1+1)(2l'_2+1)}{(2l_1+1)(2l_2+1)} \right)^{1/2} \sum_{k=0}^{\infty} \langle l'_1 k 0 0 | l_1 0 \rangle \langle l'_2 k 0 0 | l_2 0 \rangle$$

$$\times R^k(2l_1 2l_2;\, 2l'_1 2l'_2) \sum_{q=k}^{-k} (-)^q \langle l'_1 k m'_1 q | l_1 m_1 \rangle \langle l'_2 k m'_2 - q | l_2 m_2 \rangle \; , \tag{B4}$$

where the R^k are the Slater integrals[6]

$$R^k(n_1 l_1 n_2 l_2;\, n'_1 l'_1 n'_2 l'_2) = \int\!\!\int R_{n_1 l_1}(r_1) R_{n_2 l_2}(r_2)\, V_k(r_1,\, r_2)\, R_{n'_1 l'_1}(r_1) R_{n'_2 l'_2}(r_2)\, r_1^2 r_2^2\, dr_1 dr_2 \; . \tag{B5}$$

Introducing (B4) into (B2), and taking into account the definition of the unit tensor operators $\mathcal{U}^k_q(ll')$ given in (A9), we obtain immediately the two-body interaction in the form

$$\mathcal{V}=\tfrac{1}{2}\sum_{l_1 l_2}\sum_{l_1' l_2' k}\left(\frac{(2l_1'+1)(2l_2'+1)}{(2l_1+1)(2l_2+1)}\right)^{1/2}\langle l_1'k00|\,l_10\rangle$$
$$\times\langle l_2'k00|\,l_20\rangle R^k(2l_12l_2;\;2l_1'2l_2')$$
$$\times\sum_{q=k}^{-k}(-)^q\,\mathcal{U}^k_q(l_1l_1')\,\mathcal{U}^k_{-q}(l_2l_2')$$
$$-\tfrac{1}{2}\sum_{l_1l_2k}\left(\frac{2l_2+1}{2k+1}\right)\langle l_1l_200|k0\rangle^2$$
$$\times R^k(2l_12l_2;\,2l_2\,2l_1)\,\mathcal{U}^0_0(l_1l_1)\;. \tag{B6}$$

When written out in detail, this interaction appears as a linear combination of the rotation reflexion invariant operators

$$\mathcal{N},\ \mathcal{N}^2,\ \mathcal{D},\ \mathcal{D}^2,\ \mathcal{N}\mathcal{D},\ \mathcal{A}^2,\ \text{and}\ \sum(-)^q\,\mathcal{U}^2_q(11)\,\mathcal{U}^2_{-q}(11)\;.$$

It is convenient, however, to replace the last operator by the Casimir operator of the $U(3)$ group ($\mathcal{G}$) and other operators, using the formula[25]

$$\tfrac{5}{3}\sum(-)^q\,\mathcal{U}^2_q(11)\,\mathcal{U}^2_{-q}(11)=\mathcal{G}-\tfrac{1}{2}\mathcal{L}^2-\tfrac{1}{3}(\mathcal{N}-\mathcal{D})^2\;. \tag{B7}$$

$\mathcal{G}$ is diagonal in the $U(3)$ basis and its eigenvalues for the IR $(h_1h_2h_3)$ are $g=h_1^2+h_2^2+h_3^2+2h_1-2h_3$. Introducing the abbreviated notation for the Slater integrals,[6] we have the explicit form of the two-body interaction

$$\mathcal{V}=\tfrac{1}{2}F^0(2s,\,2s)\,\mathcal{D}(\mathcal{D}-1)+F^0(2s,\,2p)\,\mathcal{D}(\mathcal{N}-\mathcal{D})$$
$$+\tfrac{1}{6}G^1(2s,\,2p)(\mathcal{A}^2-\mathcal{N}-2\mathcal{D})$$
$$+\tfrac{1}{2}F^0(2p,\,2p)(\mathcal{N}-\mathcal{D})(\mathcal{N}-\mathcal{D}-1)$$
$$+\tfrac{1}{25}F^2(2p,\,2p)$$
$$\times[3\mathcal{G}-\tfrac{3}{2}\mathcal{L}^2-\mathcal{N}^2-\mathcal{D}^2+2\mathcal{N}\mathcal{D}-5\mathcal{N}+5\mathcal{D}]. \tag{B8}$$

Thus the two-body interaction appears as a linear combination of operators that are diagonal in the $U(3)$ basis: $\mathcal{D}$, $\mathcal{D}^2$, $\mathcal{N}\mathcal{D}$, and $\mathcal{G}$; an operator that is diagonal in the $O(4)$ basis: $\mathcal{A}^2$; and operators that are diagonal in both bases: $\mathcal{N}$, $\mathcal{N}^2$, and $\mathcal{L}^2$. The one-body interaction, as we saw above, is diagonal in the $U(3)$ bases. As we know the transformation coefficients of Table IV that connect the $U(3)$ and the $O(4)$ bases, we can easily construct the matrix of the Hamiltonian in any of the two bases.

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