



1977

## Group theoretical studies of the periodic chart and of configuration mixing in the ground state of helium

Yutaka Kitagawara  
*University of the Pacific*

Follow this and additional works at: [https://scholarlycommons.pacific.edu/uop\\_etds](https://scholarlycommons.pacific.edu/uop_etds)

 Part of the [Physical Sciences and Mathematics Commons](#)

---

### Recommended Citation

Kitagawara, Yutaka. (1977). *Group theoretical studies of the periodic chart and of configuration mixing in the ground state of helium*. University of the Pacific, Thesis. [https://scholarlycommons.pacific.edu/uop\\_etds/1954](https://scholarlycommons.pacific.edu/uop_etds/1954)

This Thesis is brought to you for free and open access by the Graduate School at Scholarly Commons. It has been accepted for inclusion in University of the Pacific Theses and Dissertations by an authorized administrator of Scholarly Commons. For more information, please contact [mgibney@pacific.edu](mailto:mgibney@pacific.edu).

GROUP THEORETICAL STUDIES OF THE PERIODIC  
CHART AND OF CONFIGURATION MIXING IN  
THE GROUND STATE OF HELIUM

---

A Thesis  
Presented to  
the Faculty of the Department of Physics  
College of the Pacific  
University of the Pacific

---

In Partial Fulfillment of  
the Requirements for the Degree of Master  
of Science in Physics

---

by  
Yutaka Kitagawara  
June, 1977

This thesis, written and submitted by

Yutaka Kitagawara

---

is approved for recommendation to the Committee  
on Graduate Studies, University of the Pacific.

Department Chairman or Dean:

*Andres F. Rodriguez*

---

Thesis Committee:

*Carl Wulfsberg* Chairman

---

*Bruce W. Shore*

---

*Patrick R. Jones*

---

*Robert L. Anderson*

---

Dated *June 28, 1977*

---

## ACKNOWLEDGMENT

I would like to express my deep appreciation to Professor Carl E. Wulfman for giving me a chance to study at the University of the Pacific, for his guidance, advice and ceaseless encouragement during the course of this research.

To Mr. Sukeyuki Kumei, I extend my sincere appreciation for his advice, suggestions and encouragement.

I wish to acknowledge a stimulating remark of Dr. Bruce Shore, which led to a reexamination of the results I had obtained in the final section of the first draft of the thesis and the realization that they could be much improved.

To Professor Robert Anderson, Professor Patrick Jones and Professor Andres Rodriguez, I also wish to extend my thanks for examining this thesis.

To Professor Tai-ichi Shibuya, goes my sincere appreciation for his advice and encouragement.

I wish to express my extreme gratitude to Mrs. Carl E. Wulfman for her generous hospitality during my stay at the University of the Pacific.

Finally I am deeply indebted to Miss Teang Tan and Miss Quang Huynh for typing this thesis.

## TABLE OF CONTENTS

I.	Introduction	1
II.	Effective Nuclear Charges of Electrons in Atoms and Group Theoretical Studies of the Periodic Classification of Chemical Elements	10
	2-1. General Considerations	10
	2-2. Approximate Expressions for Screening Constants of Inner and Outer Electrons in Atoms	14
	2-3. Empirical Expressions for Effective Nuclear Charges of Outer Electrons in Atoms	25
	2-4. Group Theoretical Implications of the Effective Nuclear Charge and an Idea for the Classification of Chemical Elements	31
III.	A Group Theoretical Study of Configuration Mixing for the Ground State of Helium	47
	3-1. A Physical Realization of the $SO(4,2)$ Algebra	48
	3-2. On an Approximate Dynamical Symmetry of the Helium Atom	57
	3-3. The Configuration Mixing due to several possible Two-Particle $SO(4,1)$ Symmetries and the Ground State Wave Function of the Helium Atom	64
	Appendixes	77
	References	82

## I. Introduction

In the investigation of atomic structures, the central-field model long ago proved quite successful. In this model one assumes that each electron moves in a central, or spherically symmetrical, force field, produced by the nucleus and the other electrons. Using this approximation, it was found that the Hartree-Fock method provides quite good results for atomic ground and low-excited states.<sup>(1)</sup>

Historically the central-field model for atomic structure was established as a result of the study of the periodic chart of the elements.<sup>(1)</sup> Mendelyev's discovery<sup>(2)</sup> of the periodic system of chemical elements led him to the concept of the periodic chart.

Actually the regularity of the chart can be well understood by studying the structures of inert gas atoms, which really form the key to the periodic system. During the period from 1916 to 1919, Kossel,<sup>(3)</sup> Lewis,<sup>(4)</sup> and Langmuir<sup>(5)</sup> speculated a great deal about the probable meaning of these stable inert gas structures. Langmuir particularly noted the way in which the addition of eight electrons to a helium-like ion produces neon and addition of eight to a neon-like ion produces argon. This led him to postulate a particularly stable structure of eight electrons, which

he called an octet. It was natural to think of these groups of electrons as shells of some sort and to think that one shell was completed at helium, consisting of two electrons; a second shell of eight, one of Langmuir's octets, would be completed at neon, a third shell (second octet) at argon, and so on.

With these simple ideas and fundamental facts about the periodic system in mind, Bohr<sup>(6)</sup> gave the explanation of the periodic chart in 1922, in terms of a central-field model of the atoms, coupled with a restriction on the number of electrons accommodated in a completed group. He introduced the "Aufbau" principle for elements based upon the quantum numbers  $n, l, m$  of his atomic model. For small atoms ( $Z \leq 18$ ), the orbital energy increases with increasing  $n$ , and within a given  $n$ , it increases with increasing  $l$ . Bohr's explanation was supplemented by the discovery of the electron spin by Uhlenbeck and Goudsmit<sup>(7)</sup> and of the exclusion principle by Pauli,<sup>(8)</sup> both in 1925.

However, the order in which the electron shells are successively filled for the case of neutral atoms, as  $Z$  is increased, is governed by increasing  $n+l$ , and for fixed  $n+l$ , by increasing  $n$ . This rule was first proposed by Madelung<sup>(9)</sup> as early as 1926, according to a statement published by Goudsmit.<sup>(10)</sup> In terms of Madelung's rule, the Aufbau princi-

ple mentioned above can be described by the inequalities  
 $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s.$  (1)

Spectroscopic evidence for the central-field model and Aufbau principle was first obtained during the years 1921 to 1924 from analyses of the optical spectra and X-ray spectra of sodium vapor,<sup>(11)</sup> and it is now universally accepted.

Simple approximate expressions for orbital energies in the central-field model can be realized by introducing the concept of the effective quantum number  $n^*$  and effective nuclear charge  $\zeta$ . Especially for the outermost electrons in alkali metal atoms, the optical energy levels are well expressed by

$$E = -\frac{1}{2(n^*)^2} (\text{atomic units}). \quad (2)$$

The  $n^*$  is given by  $n^* = n - d$ , where  $n$  is the principal quantum number of an electron and  $d$  is the quantum defect which is a constant characterized by each element. This approximate behavior of sodium spectra is called Rydberg's law.

Using the effective nuclear charge  $\zeta$ , the energy of an X-ray term value is approximately given by

$$E = -\frac{1}{2} \left( \frac{\zeta}{n} \right)^2 (\text{atomic units}), \quad (3)$$

where  $\zeta$  is related to the actual nuclear charge  $Z$  and the screening constant  $\sigma$ , by  $\zeta = Z - \sigma$ . This approximation corresponds to Moseley's law,<sup>(12)</sup> which says that the square roots of characteristic frequencies of X-ray spectra vary



approximately linearly with atomic number.

Once wave mechanics came along, and Hartree formulated the method of the self-consistent field (SCF),<sup>(13)</sup> one could find a central-field approximation for the energy of sodium by direct application of Hartree's method, rather than by working backward from the observed spectrum. By the improved Hartree-Fock SCF method,<sup>(14)</sup> verifications of the central-field model were made for many atoms, with results as good as those obtained for sodium.

The SCF methods provide quite good results for atomic ground and low-excited states.<sup>(1)</sup> However, sometimes it is more convenient to have simple expressions for energies and wave functions of one-electron states in terms of the  $n^*$  and  $l$  mentioned before, even if the approximations are not as good as those obtained by the SCF methods. For example, Zener<sup>(15)</sup> and Slater<sup>(16)</sup> used orbitals of the form

$$N r^{(n^*-1)} e^{-(Z-\sigma)\frac{r}{n^*}} Y_{lm}^{(w)}, \quad (5)$$

where  $n^*$  and  $\sigma$  are adjustable constants and  $N$  is a normalizing factor. These eigenfunctions are solutions of the central-field problem where the potential  $V(r)$  is given by the relation

$$V(r) = -\frac{(Z-\sigma)}{r} + \frac{n^*(n^*-1)}{2r^2}. \quad (6)$$

For large values of  $r$  this approaches

$$V(r) \sim -\frac{(Z-\sigma)}{r}, \quad (7)$$

corresponding to a screening of the nucleus equivalent to  $\sigma$ . By varying  $n^*$  and  $\sigma$  so as to minimize the energy, Slater gave a rule for determining  $n^*$  and  $\sigma$ . This is called Slater's rule. It is well known that the orbital function of Eq.(5) is frequently used for the basis for configuration interaction calculations.

In 1959, Layzer pointed out<sup>(17)</sup> that a satisfactory theory of atomic spectra should account for the simple regularities exhibited by the experimental phenomena. He mentioned that Moseley's law in X-ray spectroscopy is a surprisingly accurate approximation and a satisfactory theory should explain the  $Z$  dependence of term energies which is stated in Moseley's law. He noticed that the solution of Hartree-Fock equations for fixed values of  $Z$  already presents great difficulty for the explanation of the  $Z$ -dependence of term energies. Using a  $1/Z$ -expansion method,<sup>(18)</sup> he developed a modern screening theory of atomic spectra. His formulations are basic to the explanation of the experimental laws in X-ray spectroscopy, and he determined screening parameters  $\sigma$  by the variation principle. As he mentioned in his paper, the formulation

based on the concept of the effective nuclear charge can shift the focus of attention from individual atoms with fixed  $Z$ , to sequences of atoms. This idea may be useful for the investigation of the periodic chart.

Very recently Sternheimer<sup>(19)</sup> examined a wide range of experimental data for one-electron excited states for the valence electron of the alkali-metal atoms. He showed that in these states the orbital energy level increases with increasing Madelung's  $n+l$  except for lithium. However, for fixed  $n+l$ , the energy ordering pattern is not the Madelung's Aufbau ordering except for sodium, and the pattern is characteristic of each atom.

As we have seen above, the successful central-field model for atomic structure was established as a result of the study of the periodic chart of the elements. However, it might still be considered that the basic periodic chart itself is lacking a fully satisfactory theoretical explanation and that the Aufbau principle has not been persuasively explained. Lately, some attempts at a group theoretical derivation of the Aufbau scheme have been carried out by Barut<sup>(20)</sup> and independently by Navaro, Wolf,<sup>(21)</sup> and Berrondo, Navaro.<sup>(22)</sup>

Barut proposed that "the different elements ... (be) regarded as different states of atomic matter", and asked

"are there global quantum numbers which would characterize the elements as different states of a single system?" Considering two limiting cases, the neutral atoms and the highly ionized ones, he concluded that in both cases the one-electron orbitals of such a single system could be considered to provide a basis for a single unitary irreducible representation of the group  $SO(4,2)$ .

Navaro et al. proposed a geometrical realization of the Aufbau scheme, applying Fock's idea of the stereographic mapping of the Schrödinger equation in momentum space onto a four-dimensional hypersphere. They showed that the Aufbau ordering can be derived from the Hamiltonian of an asymmetric rotor with an  $SO(3)$  symmetry around the 4-axis on the 4-dimensional hypersphere.

Though the work of Barut and of Navaro et al. is most suggestive, it has not been given a dynamical foundation, and so is unsatisfying to the atomic physicist.

A different kind of approach to the group theoretical study of the periodic chart was attempted recently by Byakov et al.<sup>(23)</sup> They proposed  $SU(2) \times SO(4,2)$  as a dynamical group for the periodic chart. Their idea is based on the fact that the system of chemical elements can be classified by an  $SO(4,2)$  orbital labeling scheme using the hydrogenic quantum numbers

$n, l, m$  and an  $SU(2)$  quantum number. However, here again no dynamical foundation has been provided for the group proposed.

Recently Wulfman found great merit in Barut's idea on atomic super-multiplets, and he introduced the concept of the generalized Hamiltonian that is the Hamiltonian of all atoms.<sup>(24)</sup>

Investigating the Schrödinger equation with this generalized Hamiltonian, it should be possible to relate the properties of different atoms and find the structure of the periodic chart from fundamental principles of dynamics and group theory. One can use the same kinds of methods for relating the properties of different states of a single hydrogen atom with the aid of the degeneracy group  $SO(4)$  and dynamical group  $SO(4,2)$ . These groups represent the symmetries of the time-independent and time-dependent Schrödinger equations with ordinary Hamiltonian.<sup>(25,26)</sup> The idea then is to apply these methods to the system defined by a generalized Hamiltonian.

In chapter II of this thesis, we will consider the classification of chemical elements, in the light of the concept of the generalized Hamiltonian. We will make a group theoretical classification based on the characteristics of the outermost electrons in the central-field model of atomic ground states. We conclude that the classification group may be  $SO(p,q)$  with  $p+q \geq 7$ ,  $p \geq 4$ .

In the problems of atomic physics, we may find a number of unsolved problems in addition to the problem of the periodic chart just discussed. One of the problems is to establish, from first principles, simpler approximation methods for many-electron problems. It is well known that configuration interaction calculations for the atomic ground states of small atoms have been quite successful.<sup>(27)</sup> However, we would like to predict these configuration mixings in simpler ways. Recently Wulfman and Kumei<sup>(28)</sup> examined the matrix elements of the  $1/r_{12}$  electron repulsion potential expressed in terms of the generators of the dynamical group  $SO(4,2)$ . From this investigation Wulfman found an approximate dynamical symmetry of doubly excited states of the helium atom.<sup>(29)</sup> More extensive calculations by Sinanoğlu and Herrick showed the idea was even more successful than at first realized.<sup>(30)</sup> However this method cannot be applied to the states in which one or more electrons have principal quantum number  $n=1$ .<sup>(30)</sup>

In chapter III of this thesis, we will review Wulfman's work briefly and consider an application of his idea to the ground state of helium making use of the group  $SO(4,1) \times SO(4,1)$ . We arrive at the conclusion that we can obtain physically significant configuration mixing using  $SO(4,1) \times SO(4,1)$  or  $SO(4,2) \times SO(4,2)$  in a manner analogous to the way in which  $SO(4) \times SO(4)$  is used to determine configuration mixing in doubly excited states of helium-like systems.

## II. Effective Nuclear Charges of Electrons in Atoms and Group Theoretical Studies of the Periodic Classification of Chemical Elements

### 2-1. General Considerations

We know the periodic chart has a very beautiful structure, and it would be quite significant to have a simple explanation of the classification it provides. In order to study the structure of the chart, we should have a simple mathematical expression which well characterizes the electronic energy of ground and low lying excited states of all the chemical elements. It may be proper to obtain this from simple SCF one-electron wave functions which can be approximated by hydrogenic wave functions with effective nuclear charges  $\zeta$  which will be a function of the actual nuclear charge  $Z$ . The expression for  $\zeta$  should be common for all the elements. Studying such a simple approximate expression of one-electron states, we may find clues to the dynamical and group theoretical origins of the chart.

Recently Wulfman introduced a quite unique group theoretical methodology<sup>(24)</sup> to investigate systems whose Hamiltonians are related to one another by varying a parameter. In the context here his idea is the following.

First he defines a "third quantized" Hamiltonian that is the Hamiltonian of all atoms, in a sense analogous to the sense in which the ordinary Hamiltonian is the Hamiltonian of all states of a single atom. Given such a third quantized Hamiltonian one can bring to bear upon the problem of relating the properties of different atoms all those techniques which are currently available for relating the properties of different states of the same atom. For the simple SCF one-electron state such a Hamiltonian can be realized as

$$H = \frac{p^2}{2} - \frac{Z_{op}}{r}, \quad (1)$$

with a new type of "third quantized" one-electron wave function  $\Psi$  which satisfies

$$Z_{op} \Psi = Z \Psi. \quad (2)$$

Here  $Z_{op}$  is an effective nuclear charge operator which produces a proper effective nuclear charge when operating on its eigenfunction  $\Psi$ . For example let  $Z_{op} = i \frac{\partial}{\partial S}$ ,  $\Psi = e^{-iS} \phi(\vec{r}, t)$ , then we have  $i \frac{\partial}{\partial S} \Psi = Z \Psi$ .

For the investigation of the chart, it will be most important to think about outer (shell) electrons,\*

---

\* The definition of outer electrons is given in section 2-3; p. 25.



because the characteristics of each chemical element strongly depend on the behaviour of these electrons. Furthermore we may say the group structure of the periodic chart is determined by the group properties of outer electrons in atomic ground states. Therefore we should think about a simple SCF one-electron state for the outer electron for which Eqs. (1) and (2) are written as the third quantized forms.

$$H_{o.e} = \frac{p^2}{2} - \frac{(\zeta_{o.e})_{op}}{r} \quad (3)$$

$$(\zeta_{o.e})_{op} \psi_{o.e} = \zeta_{o.e} \psi_{o.e} \quad (4)$$

In principle then we would obtain a basic group theoretical structure of the periodic chart by studying the invariance group of the differential equation

$$\left\{ \frac{p^2}{2} - \frac{(\zeta_{o.e})_{op}}{r} - i \frac{\partial}{\partial t} \right\} \psi_{o.e} = 0, \quad (5)$$

where  $\psi_{o.e} = f_{o.e}(s) \phi_{o.e}(\vec{r}) e^{-iE_{o.e}t}$ , (6)

$$E_{o.e} = -\frac{1}{2} \left( \frac{\zeta_{o.e}}{n_{o.e}} \right)^2 = \left( \text{one-electron energy of the outer electron} \right), \quad (7)$$

$$(\zeta_{o.e})_{op} f_{o.e}(s) = \zeta_{o.e} f_{o.e}(s), \quad \left( \frac{p^2}{2} - \frac{\zeta_{o.e}}{r} \right) \phi_{o.e}(\vec{r}) = E_{o.e} \phi_{o.e}(\vec{r}). \quad (8)$$

The invariance group of Eq. (5) generated by operators

$Q(r, s, t, \frac{\partial}{\partial r}, \frac{\partial}{\partial s}, \frac{\partial}{\partial t}, \dots)$  can be obtained by studying the equation

$$\left\{ \frac{p^2}{2} - \frac{(\zeta_{o.e})_{op}}{r} - i \frac{\partial}{\partial t} \right\} Q \psi_{o.e} = 0, \quad (9)$$

using the method given by Anderson, Kumei and Wulfman. (31,32,25)  
 States labeled by  $\zeta_{o.e}, n_{o.e}$  will be degenerate if  $(\zeta_{o.e}/n_{o.e}) =$   
 constant. The group that interconverts such states is the  
 degeneracy group of the third quantized system. We suppose  
 it to be a subgroup of the dynamical group which interconverts  
 all states of the third quantized system.

Therefore our first task is to obtain common expres-  
 sion of the effective nuclear charge  $\zeta$  as simply as possible.  
 We will obtain some of them in section 2-2 and 2-3. However  
 we will find that it is unhelpful to carry out the problem in  
 the way mentioned above, because the expression for  $\zeta$  can not  
 be simple enough to investigate Eq.(9). Nevertheless the  
 expression of  $\zeta$  will still give us some useful group theo-  
 retical information that will give us an idea for the classi-  
 fication of chemical elements. This will be discussed in  
 section 2-4.

## 2-2. Approximate Expressions for Screening Constants of Inner and Outer Electrons in Atoms

In this section we try to obtain some simple approximate expressions for screening constants of electrons in atoms. Screening constants can be obtained by minimizing the energy expectation value by variation of the screening parameters. However the expression so obtained is always quite complicated. In order to be useful the expression obtained should be quite simple. To this end we shall ignore the antisymmetry of the wave function and make a special simplification for the electron repulsion term.

In a nonrelativistic approximation the Hamiltonian for an N-electron atom of nuclear charge Z is given by

$$H = \sum_{j=1}^N \left\{ \frac{P_j^2}{2} - \frac{Z}{r_j} \right\} + \sum_{j < k} \frac{1}{r_{jk}} . \quad (10)$$

We assume the following wave function:

$$\begin{aligned} \Phi &= \psi_{\alpha_a l_a m_a}(\alpha_a \vec{r}_1 / m_a) \psi_{\alpha_b l_b m_b}(\alpha_b \vec{r}_2 / m_b) \cdots \psi_{\alpha_p l_p m_p}(\alpha_p \vec{r}_N / m_p) \\ &\equiv U_{\alpha}(\vec{r}_1) U_{\beta}(\vec{r}_2) \cdots U_{\rho}(\vec{r}_N) \end{aligned} \quad (11)$$

$U_{\alpha}(\vec{r}_i)$  are ordinary hydrogenic wave functions defined by

$$\begin{aligned}
 u_z(\vec{r}_i) &\equiv \psi_{n_z l_z m_z}(\alpha_z \vec{r}_i / n_z) \\
 &= \frac{1}{(2l_z+1)!} \sqrt{\frac{(2\alpha_z)^3 (n_z+l_z)!}{n_z! 2n_z(n_z-l_z-1)!}} e^{-\alpha_z r_i / n_z} (2\alpha_z r_i / n_z)^{l_z} F(-n_z+l_z+1, 2l_z+2; 2\alpha_z r_i / n_z) Y_{l_z m_z}^{(\omega_i)}.
 \end{aligned}
 \tag{12}$$

The  $\alpha_z$  are variation parameters. For the minimum of the expectation value of the Hamiltonian,  $\alpha_z$  become suitable effective nuclear charges  $\zeta_z$ . Eq.(10) can be rewritten as

$$\begin{aligned}
 H &= \{H_a^{(1)} + H_b^{(2)} + \dots + H_p^{(N)}\} \\
 &\quad - \left\{ (Z-\alpha_a) \frac{1}{r_1} + (Z-\alpha_b) \frac{1}{r_2} + \dots + (Z-\alpha_p) \frac{1}{r_N} \right\} + \sum_{j < k} \frac{1}{r_{jk}},
 \end{aligned}
 \tag{13}$$

where  $H_z^{(j)} \equiv \left( \frac{p_j^2}{2} - \frac{\alpha_z}{r_j} \right)$ .

Using the wave function(11), the expectation value of the Hamiltonian is expressed as the following.

$$\begin{aligned}
 E &= \iiint \Phi^* H \Phi \cdot d^3\vec{r}_1 \cdot d^3\vec{r}_2 \\
 &= \left\{ \int u_a^*(\vec{r}_1) H_a^{(1)} u_a(\vec{r}_1) d^3\vec{r}_1 + \int u_b^*(\vec{r}_2) H_b^{(2)} u_b(\vec{r}_2) d^3\vec{r}_2 + \dots + \int u_p^*(\vec{r}_N) H_p^{(N)} u_p(\vec{r}_N) d^3\vec{r}_N \right\} \\
 &\quad - \left\{ (Z-\alpha_a) \int u_a^*(\vec{r}_1) \frac{1}{r_1} u_a(\vec{r}_1) d^3\vec{r}_1 + (Z-\alpha_b) \int u_b^*(\vec{r}_2) \frac{1}{r_2} u_b(\vec{r}_2) d^3\vec{r}_2 + \dots + (Z-\alpha_p) \int u_p^*(\vec{r}_N) \frac{1}{r_N} u_p(\vec{r}_N) d^3\vec{r}_N \right\} \\
 &\quad + \frac{1}{2} \sum_{\eta, \xi} \iint u_\eta^*(\vec{r}_\eta) u_\xi^*(\vec{r}_\xi) \frac{1}{r_{\eta\xi}} u_\eta(\vec{r}_\eta) u_\xi(\vec{r}_\xi) d^3\vec{r}_\eta d^3\vec{r}_\xi.
 \end{aligned}
 \tag{14}$$

$$(\eta, \xi = a, b, c, \dots, p)$$

The one-particle integrations are easily carried out.

$$\int u_z^*(\vec{r}_j) H_z(\omega) u_z(\vec{r}_j) \cdot d^3\vec{r}_j = -\frac{1}{2} \frac{\alpha_z^2}{n_z^2} .$$

$$\int u_z^*(\vec{r}_j) \frac{1}{r_j} u_z(\vec{r}_j) \cdot d^3\vec{r}_j = \frac{\alpha_z}{n_z^2} .$$

In order to have a simple expression for the electron repulsion integral, we will use a special technique of Wulfman and Kumei. (28) Let us introduce the following operator and function.

$${}^jT_2 = -i \left( r_j \frac{\partial}{\partial r_j} + 1 \right) ,$$

$$\chi_{n_z l_z m_z}(\vec{r}_j) = \frac{2}{(2l_z+1)! (n_z-l_z-1)!} \sqrt{\frac{(n_z+l_z)!}{(n_z-l_z)!}} e^{-r_j} (2r_j)^{l_z} F(-n_z+l_z+1, 2l_z+2; 2r_j) \cdot Y_{l_z m_z}(\omega_j) .$$

(15)

The hydrogenic wave function can be expressed as \*

$$u_z(\vec{r}_j) = \psi_{n_z l_z m_z}(\alpha_z \vec{r}_j / n_z) = \frac{\sqrt{\alpha_z}}{n_z} e^{i\theta_z ({}^jT_2)} \chi_{n_z l_z m_z}(\vec{r}_j) , \quad \theta_z = \ln \left( \frac{\alpha_z}{n_z} \right) .$$

The repulsion integral can be written as

$$\begin{aligned} V_{q\bar{s}} &\equiv \iint u_q^*(\vec{r}_j) u_{\bar{s}}^*(\vec{r}_k) \frac{1}{r_{jk}} u_q(\vec{r}_j) u_{\bar{s}}(\vec{r}_k) \cdot d^3\vec{r}_j d^3\vec{r}_k \\ &= \iint u_q^*(\vec{r}_j) u_{\bar{s}}^*(\vec{r}_k) \frac{r_j r_k}{r_{jk}} u_q(\vec{r}_j) u_{\bar{s}}(\vec{r}_k) \cdot r_j d\omega_j \cdot r_k d\omega_k \\ &\equiv \left\langle u_q(\vec{r}_j) u_{\bar{s}}(\vec{r}_k) \left| \frac{r_j r_k}{r_{jk}} \right| u_q(\vec{r}_j) u_{\bar{s}}(\vec{r}_k) \right\rangle \end{aligned}$$

\* See p.52-53.

$$\begin{aligned}
&= \frac{\alpha_4 \alpha_5}{(n_4 n_5)^2} \left\langle \chi_{n_4 l_4 m_4}^{(\vec{r}_i)} \chi_{n_5 l_5 m_5}^{(\vec{r}_k)} \middle| \frac{\tilde{r}_i \tilde{r}_k}{\tilde{r}_{jk}} \middle| \chi_{n_4 l_4 m_4}^{(\vec{r}_i)} \chi_{n_5 l_5 m_5}^{(\vec{r}_k)} \right\rangle \\
&\equiv \frac{\alpha_4 \alpha_5}{(n_4 n_5)^2} \langle \eta_{\mathbb{F}} | \tilde{r}_i \tilde{r}_k (\tilde{r}_{jk})^{-1} | \eta_{\mathbb{F}} \rangle,
\end{aligned} \tag{16}$$

where 
$$\tilde{r} = e^{-i\theta_4({}^j T_2)} e^{-i\theta_5({}^k T_2)} r e^{i\theta_4({}^j T_2)} e^{i\theta_5({}^k T_2)}.$$

Wulfman and Kumei showed <sup>(28)</sup>  $V_{\eta_{\mathbb{F}}}$  can be expanded as

$$\begin{aligned}
V_{\eta_{\mathbb{F}}} &= \frac{\alpha_4 \alpha_5}{(n_4 n_5)^2} \langle \eta_{\mathbb{F}} | (\tilde{r}_j^2 + \tilde{r}_k^2)^{-1/2} \tilde{r}_j \tilde{r}_k (1 + \frac{1}{2}R + \frac{3}{8}R^2 + \dots) | \eta_{\mathbb{F}} \rangle \\
&\approx \frac{\alpha_4 \alpha_5}{(n_4 n_5)^2} \frac{\langle \eta_{\mathbb{F}} | \tilde{r}_j \tilde{r}_k | \eta_{\mathbb{F}} \rangle}{\left\{ \langle \eta_{\mathbb{F}} | \tilde{r}_j^2 + \tilde{r}_k^2 | \eta_{\mathbb{F}} \rangle \right\}^{1/2}} \left[ 1 + \frac{3}{8} \frac{\langle \eta_{\mathbb{F}} | (2\tilde{r}_j \cdot \tilde{r}_k)^2 | \eta_{\mathbb{F}} \rangle}{\left\{ \langle \eta_{\mathbb{F}} | \tilde{r}_j^2 + \tilde{r}_k^2 | \eta_{\mathbb{F}} \rangle \right\}^2} + \dots \right],
\end{aligned} \tag{17}$$

where 
$$R = (2\tilde{r}_j \cdot \tilde{r}_k) (\tilde{r}_j^2 + \tilde{r}_k^2)^{-1}.$$

If we only consider the first dominant term in (17), we can get a quite simple expression of  $V_{\eta_{\mathbb{F}}}$

$$\begin{aligned}
V_{\eta_{\mathbb{F}}} &\approx \frac{\alpha_4 \alpha_5}{(n_4 n_5)^2} \frac{\langle \eta_{\mathbb{F}} | \tilde{r}_j \tilde{r}_k | \eta_{\mathbb{F}} \rangle}{\left\{ \langle \eta_{\mathbb{F}} | \tilde{r}_j^2 + \tilde{r}_k^2 | \eta_{\mathbb{F}} \rangle \right\}^{1/2}} = \frac{1}{\left\{ \langle \eta_{\mathbb{F}} | \tilde{r}_j^2 + \tilde{r}_k^2 | \eta_{\mathbb{F}} \rangle \right\}^{1/2}} \\
&= \sqrt{2} \left[ \left( \frac{n_4}{\alpha_4} \right)^2 \{ 3n_4^2 - l_4(l_4+1) \} + \left( \frac{n_5}{\alpha_5} \right)^2 \{ 3n_5^2 - l_5(l_5+1) \} \right]^{-1/2}
\end{aligned} \tag{18}$$

The approximation given by (18) is not so good because Eq. (17) does not converge rapidly, but for our purpose the simplicity of the expression is quite important. Using the result of (18) we write the energy expectation value as

$$E \approx -\frac{1}{2} \sum_{\mu} \left( \frac{\alpha_{\mu}}{n_{\mu}} \right)^2 - \sum_{\mu} (Z - \alpha_{\mu}) \frac{\alpha_{\mu}}{n_{\mu}^2} + \frac{1}{\sqrt{2}} \sum_{\substack{\mu, \nu \\ (\mu \neq \nu)}} \left[ \left( \frac{n_{\mu}}{\alpha_{\mu}} \right)^2 \{3n_{\mu}^2 - l_{\mu}(l_{\mu} + 1)\} + \left( \frac{n_{\nu}}{\alpha_{\nu}} \right)^2 \{3n_{\nu}^2 - l_{\nu}(l_{\nu} + 1)\} \right]^{-1/2} \quad (19)$$

$$\begin{cases} \mu, \nu = a, b, c, \dots, p \\ a = (n_a l_a m_a m_{s_a}) \text{ etc.} \end{cases}$$

We now minimize Eq.(19) by requiring  $\frac{\partial E}{\partial \alpha_a} \approx 0$ .

Setting  $\alpha_{\tau} = Z - \sigma_{\tau} = Z(1 - \beta_{\tau})$ , we have

$$\frac{(1 - \beta_a)}{n_a^2} - \frac{1}{n_a^2} + \frac{\sqrt{2}}{Z} \cdot M_a \sum_{\substack{\mu \\ (\mu \neq a)}} (1 - \beta_{\mu})^3 \left[ (1 - \beta_{\mu})^2 M_a + (1 - \beta_a)^2 M_{\mu} \right]^{-3/2} \approx 0, \quad (20)$$

where  $M_{\tau} = n_{\tau}^2 \{3n_{\tau}^2 - l_{\tau}(l_{\tau} + 1)\}$ ,  $\beta_{\tau} = \frac{\sigma_{\tau}}{Z}$ . (21)

$\sigma_{\tau}$  is a screening constant for the electron whose quantum state is  $\tau = (n_{\tau} l_{\tau} m_{\tau} m_{s_{\tau}})$ . We rewrite (20) as

$$\sigma_a \approx \sqrt{2} n_a^2 M_a \sum_{\substack{\mu \\ (\mu \neq a)}} \left\{ M_a + \left( \frac{Z - \sigma_a}{Z - \sigma_{\mu}} \right)^2 M_{\mu} \right\}^{-3/2} \quad (22)$$

In order to calculate  $\sigma_a$ , we have to know the screening constants for all the electrons in atoms. Tentatively let us use the screening constants obtained by Slater's rules<sup>(16)</sup> to calculate  $\left( \frac{Z - \sigma_a}{Z - \sigma_{\mu}} \right)^2$ , that is, let us see whether

$$\sigma_a \approx \sigma_a^{(n)} \equiv \sqrt{2} n_a^2 M_a \sum_{\substack{\mu \\ (\mu \neq a)}} \left\{ M_a + \left( \frac{Z - \sigma_a^{sl}}{Z - \sigma_{\mu}^{sl}} \right)^2 M_{\mu} \right\}^{-3/2}, \quad (23)$$

where  $\sigma_{\tau}^{sl}$  are Slater's screening constants. The  $\sigma_a^{(1)}$  obtained for outer electrons are plotted in Fig.1, being compared with  $\sigma_a^{sl}$  and  $\sigma_a^{ex}$ . The  $\sigma_a^{ex}$  are defined by

$$T_a = -\frac{1}{2} \frac{(Z - \sigma_a^{ex})^2}{n_a^2} \quad \sigma_a^{ex} = Z - n_a \sqrt{-2T_a}, \quad (24)$$

where  $T_a$  are experimentally determined<sup>(33)</sup> one-electron energies of  $(n_a l_a m_a m_{s_a})$ . Looking at Fig.1 we may say the  $\sigma_a^{sl}$  approximately satisfy Eq.(22) for small atoms ( $Z=1\sim 18$ ). Even if the  $\sigma_a^{sl}$  take closer values to the  $\sigma_a^{ex}$  than the  $\sigma_a^{(1)}$  do, in a sense the solutions of Eq.(22) have better characteristics than Slater's screening constants, because the  $n_a, l_a$  dependencies are taken into account in Eq.(22) but not in Slater's rule. For larger atoms ( $Z>18$ ) Eq.(22) is not reasonable at all.

From the graph it appears however that it may be possible to get a good approximate equation by introducing two parameters  $\epsilon_{in}$  and  $\epsilon_{out}$ , with

$$\sigma_a \approx \sqrt{2} n_a^2 M_a \left[ \sum_{\mu}^{(D_{n_a l_a} \leq D_{n_a l_a})} \{M_a + \epsilon_{in} M_{\mu}\}^{-\frac{3}{2}} + \sum_{\mu}^{(D_{n_a l_a} > D_{n_a l_a})} \{M_a + \epsilon_{out} M_{\mu}\}^{-\frac{3}{2}} \right]. \quad (25)$$

$D_{n_a l_a}$  is defined by  $D_{n_a l_a} = \frac{n_a(n_a-1)}{2} + l_a$  and takes

the following values:

$n_{\tau}$	1	2	2	3	3	3	...
$l_{\tau}$	0	0	1	0	1	2	...
$D_{n_{\tau} l_{\tau}}$	0	1	2	3	4	5	...



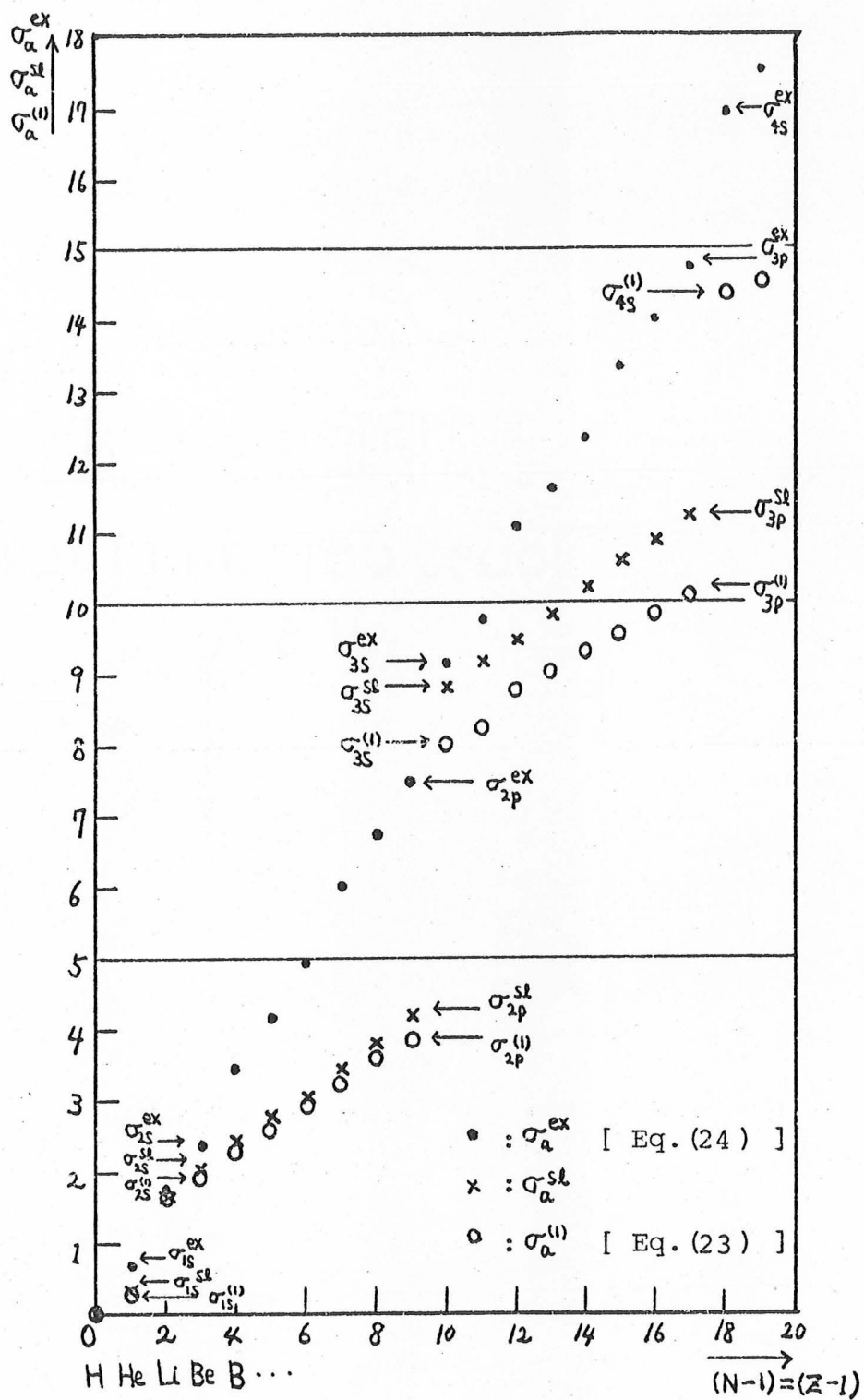


Fig. 1

For  $\epsilon_{in} = 0$ ,  $\epsilon_{out} \equiv \epsilon = 0.13$ , Eq. (25) becomes

$$\sigma_a \approx \sigma_a^{(2)} \equiv \sqrt{2} n_a^2 \left[ (N'-1) M_a^{-1/2} + M_a \sum_{\substack{\mu \\ (D_{n_a l_a} > D_{n_a l_\mu})}} \{M_a + \epsilon M_\mu\}^{-3/2} \right], \quad (26)$$

where  $N'$  is the number of electrons whose  $D_{n_\mu l_\mu}$  are smaller than or equal to  $D_{n_a l_a}$ . In Fig. 2 the result of Eq. (26) is given, being compared with  $\sigma_a^{ex}$ . Looking at Fig. 2 we may say Eq. (26) well characterizes the  $n_a, l_a$  dependency of the screening constants, but the approximation is not so good especially for electrons whose principal quantum numbers  $n_a$  are large. For the improvement of Eq. (26) we will introduce a correction term as

$$\sigma_a \approx \sigma_a^{(2)} \equiv \sqrt{2} n_a^2 \left[ (N'-1) M_a^{-1/2} + M_a \sum_{\substack{\mu \\ (D_{n_a l_a} > D_{n_a l_\mu})}} \{M_a + \epsilon M_\mu\}^{-3/2} \right] + \gamma (n_a - 1)^\xi \quad (27)$$

where  $\epsilon, \gamma, \xi$  should be determined so that (27) might give a good approximation. If we set  $\epsilon = 0.166$ ,  $\gamma = 0.247$ ,  $\xi = 1.924$ , we will have the result in Fig. 3. We may say Eq. (27) well characterizes the  $n_a, l_a$  dependency of the screening constants especially for outer shell electrons of atoms whose atomic numbers are  $1 \sim 36$ .

Let us summarize our discussion up to this point in group theoretical language. As I showed in page 14-15, we have used the hydrogenic wavefunctions with scale parameters  $\alpha_\tau$ :

$$\psi_{n_\tau l_\tau m_\tau}(\alpha_\tau \vec{r}_i / n_\tau) = \frac{\sqrt{\alpha_\tau}}{n_\tau} e^{i\theta_\tau(jT_2)} \chi_{n_\tau l_\tau m_\tau}(\vec{r}_i), \quad (28)$$

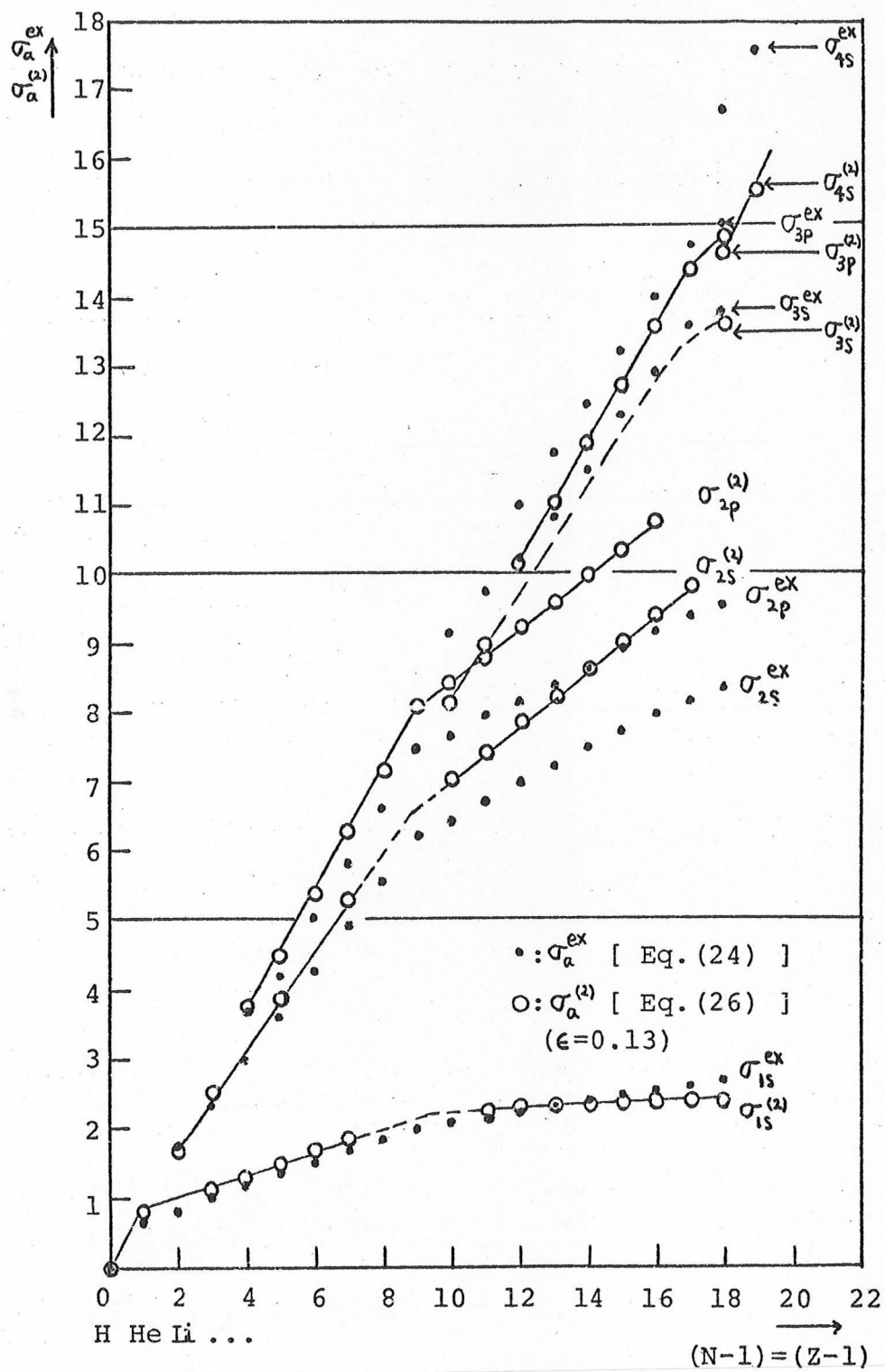


Fig. 2

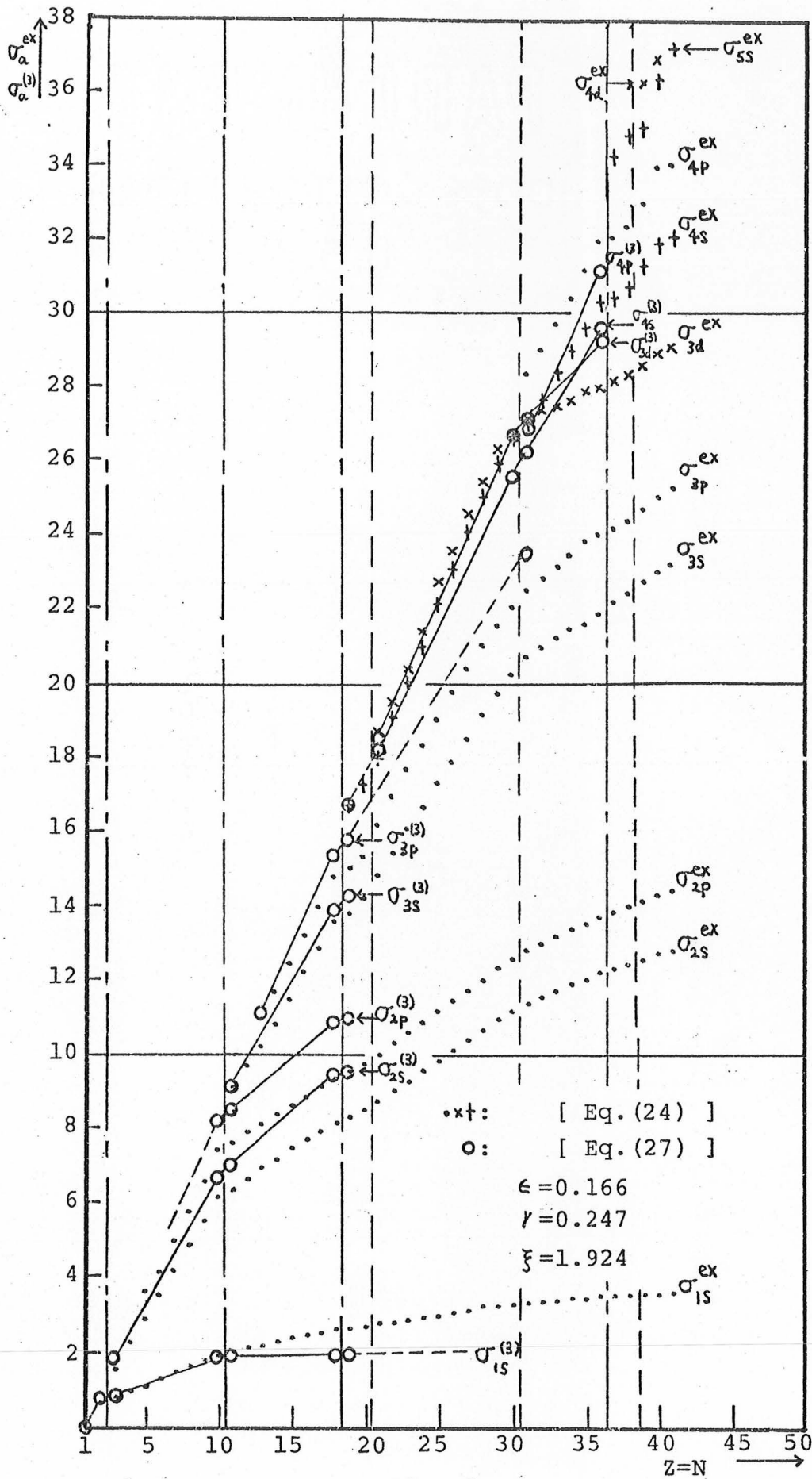


Fig. 3

where  $jT_2$  is one of the generators of  $jSO(4,2)^*$  and  $e^{i\theta_T(jT_2)}$  are dilation transformation operators. Starting from the  $jSO(4,2)$  basis functions  $\chi_{n_r l_r m_r}^{(\vec{r})}$ , we have used the dilation transformations of  $jSO(4,2)$  to determine effective nuclear charges by minimizing the expectation value  $E$  with respect to variations in the dilation parameters  $\theta_T$ . We also have used a simple  $SO(4,2)$  approximation<sup>(28)</sup> for the electron repulsion integrals. It is evident that even with the simple approximation used, we have obtained screening constants which characterize some features of the behavior of outer shell electrons in small atoms, for instance the approximate degeneracy pattern of 4s and 3d outer shell electrons is taken into account in the expression of  $\sigma_a^{(3)}$  (see Fig.3.).

---

\* In section 3-1 we display the generators of the dynamical group  $SO(4,2)$  in the realization due to Bednár et al.<sup>(43,44,45)</sup>

### 2-3. Empirical Expressions for Effective Nuclear Charges of Outer Electrons in Atoms.

In the previous section we obtained some approximate equations for screening constants of inner and outer electrons, but they are not convenient for atoms of large atomic number. However it is very important for the investigation of the periodic chart to know the relationship between atomic numbers and effective nuclear charges of outer electrons in a wide range of atomic numbers. Now we are going to obtain a simple expression for effective nuclear charges which well characterizes the periodicity in the periodic chart. In order to obtain a simple form we would rather start from experimental data than from theoretical equations. The proper effective nuclear charges of outer electrons will be experimentally determined as

$$\frac{1}{2} \left( \frac{Z_{o.e}^{ex}}{n_{o.e}} \right)^2 = \frac{(I.P.)}{27.21} \quad \text{or} \quad \left( \frac{Z_{o.e}^{ex}}{n_{o.e}} \right) = \sqrt{\frac{2(I.P.)}{(27.21)}} \quad , \quad (29)$$

where  $Z_{o.e}^{ex}$  and  $n_{o.e}$  are effective nuclear charges and principal quantum numbers of outer electrons which are most easily ionized, (I.P.) represents first ionization potentials expressed in eV . In this section outer electrons mean the electrons which have the highest or second highest value

of  $D_{n_r l_r} \equiv \frac{n_r(n_r-1)}{2} + l_r^*$  ; e.g. 2s, 2p electrons for B; 3d, 4s electrons for Sc, etc. Here it should be noticed that the outer electrons are characterized by a quantum number

$$\begin{aligned} \nu &= n_{o.e} + |l_{o.e} - \frac{1}{2}| - \frac{1}{2} \\ &= n_{o.e} + l_{o.e} + \delta_{l_{o.e}, 0} - 1 \end{aligned} \quad (30)$$

Thus  $\nu$  is an outer shell labeling number which takes the values 1, 2, 3, ... for outer shells K, L, M, .... The data of the first ionization potentials and the corresponding  $(\zeta_{o.e}^{ex} / n_{o.e})$  are listed in Appendix I, and the values of  $(\zeta_{o.e}^{ex} / n_{o.e})$  are plotted in Fig. 4 (page 30).

Looking at Fig. 4 we may notice that a first approximation may be made by making straight lines through points which represent the  $(\zeta_{o.e}^{ex} / n_{o.e})$  for alkali metal atoms and rare gas atoms. These are drawn in Fig. 4 by broken lines. This simple expression does not have a proper  $l_{o.e}$  dependency, nevertheless it is desirable for the theoretical investigation of the periodicity of the periodic chart because of its simplicity. Let us try to make a simple equation which

---

*	$n_r$	1	2	2	3	3	3	...
	$l_r$	0	0	1	0	1	2	...
	$D_{n_r l_r}$	0	1	2	3	4	5	...

approximately represents the broken lines in Fig.4. Our equation should be written as

$$\left(\frac{I_{0.e}}{n_{0.e}}\right) = k(\nu) \cdot N + d(\nu), \quad (31)$$

where the slopes  $k(\nu)$  and the intercepts  $d(\nu)$  are expressed as functions of  $\nu$ . We notice that the slopes of the broken lines are about the same for L and M shells, N and O shells, P and Q shells. It is due to the fact that L, N, P shells have almost the same electronic structures as M, O, Q shells. It is reasonable to have the relations  $k(2)=k(3)$ ,  $k(4)=k(5)$ ,  $k(6)=k(7), \dots$ , and the  $k(\nu)$  should be well expressed using the quantity  $\mu(\nu)$  defined by

$$\mu(\nu) \equiv \nu \{ \nu + (-1)^\nu \}, \quad (32)$$

which satisfy the relations  $\mu(2)=\mu(3)$ ,  $\mu(4)=\mu(5)$ ,  $\mu(6)=\mu(7), \dots$ . Using the  $\mu(\nu)$  we will write the  $k(\nu)$  as

$$k(\nu) = \frac{(0.496)}{\mu(\nu) + (1.442)} \quad (33)$$

which is a good approximation for the slopes.

Now we would like to obtain intercepts  $d(\nu)$ . Looking at Fig.4 we will notice that the curve through rare gas elements can be well approximated as

$$P(N) = \frac{(14.0)}{N + (22.5)} + (0.774). \quad (34)$$



If we know a simple approximate expression  $N_0$  for the atomic numbers of rare gas atoms, we can easily write the  $(\zeta_{0,e}/n_{0,e})$  as

$$\left\{ \left( \frac{\zeta_{0,e}}{n_{0,e}} \right) - P(N_0) \right\} = k(\nu) \{ N - N_0 \},$$

or 
$$\left( \frac{\zeta_{0,e}}{n_{0,e}} \right) = k(\nu) \{ N - N_0 \} + P(N_0). \quad (35)$$

Looking at the electron configuration scheme for atoms, we know that p, d, f electrons first appear at  $N=5, 21, 58$  (B, Sc, Ce), and notice the atomic numbers of rare gas atoms are closely related to these numbers. The Thomas-Fermi approximation predicts<sup>(34)</sup> that these numbers will be given as  $(0.17)(2l+1)^3$  where  $l$  is the azimuthal quantum number of the electron which first appears in the atom. Using this fact we can construct the following equation\* which gives us a simple approximate expression for atomic numbers of rare gas atoms.

$$N_0 = 0.17(\nu+2)^3 - \{ 1.9 + 0.7(-1)^{\nu+1} \}. \quad (36)$$

From Eqs. (32) ~ (36), we have

$$\begin{aligned} \left( \frac{\zeta_{0,e}}{n_{0,e}} \right) &= \frac{(0.496)}{\nu \{ \nu + (-1)^\nu \} + (1.442)} \left\{ N - 0.17(\nu+2)^3 + \{ 1.9 + 0.7(-1)^{\nu+1} \} \right\} \\ &+ \frac{(14.0)}{0.17(\nu+2)^3 - \{ 1.9 + 0.7(-1)^{\nu+1} \} + 22.5} + (0.794). \end{aligned} \quad (37)$$

---

\* See Appendix II.

The results of Eqs. (32) ~ (36) are listed on the following table, and the  $(\sum_{o.e} / n_{o.e})$  are plotted in Fig.4.

$\nu$	1	2	3	4	5	6	7							
$\mu(\nu)$	0	6		20		42								
$k(\nu)$	0.344	0.0666		0.0231		0.01142								
$N_o$	2.0	9.7	18.6	35.5	55.7	85.8								
$P(N_o)$	1.344	1.209	1.115	1.015	0.953	0.903								
$N$	1	2	3	10	11	18	19	36	37	54	55	86		
$(\sum_{o.e} / n_{o.e})$	1.000	1.344	0.961	1.228	0.607	1.074	0.633	1.026	0.520	0.913	0.551	0.905		

It is evident that Eq. (37) is a much better approximation than Eq. (27) in the previous section for outermost electrons, and it has important characteristics of the periodic chart because of the term  $\nu\{\nu + (-1)^\nu\}$ . In the following section we will give some discussions of the group theoretical implications of this observation.

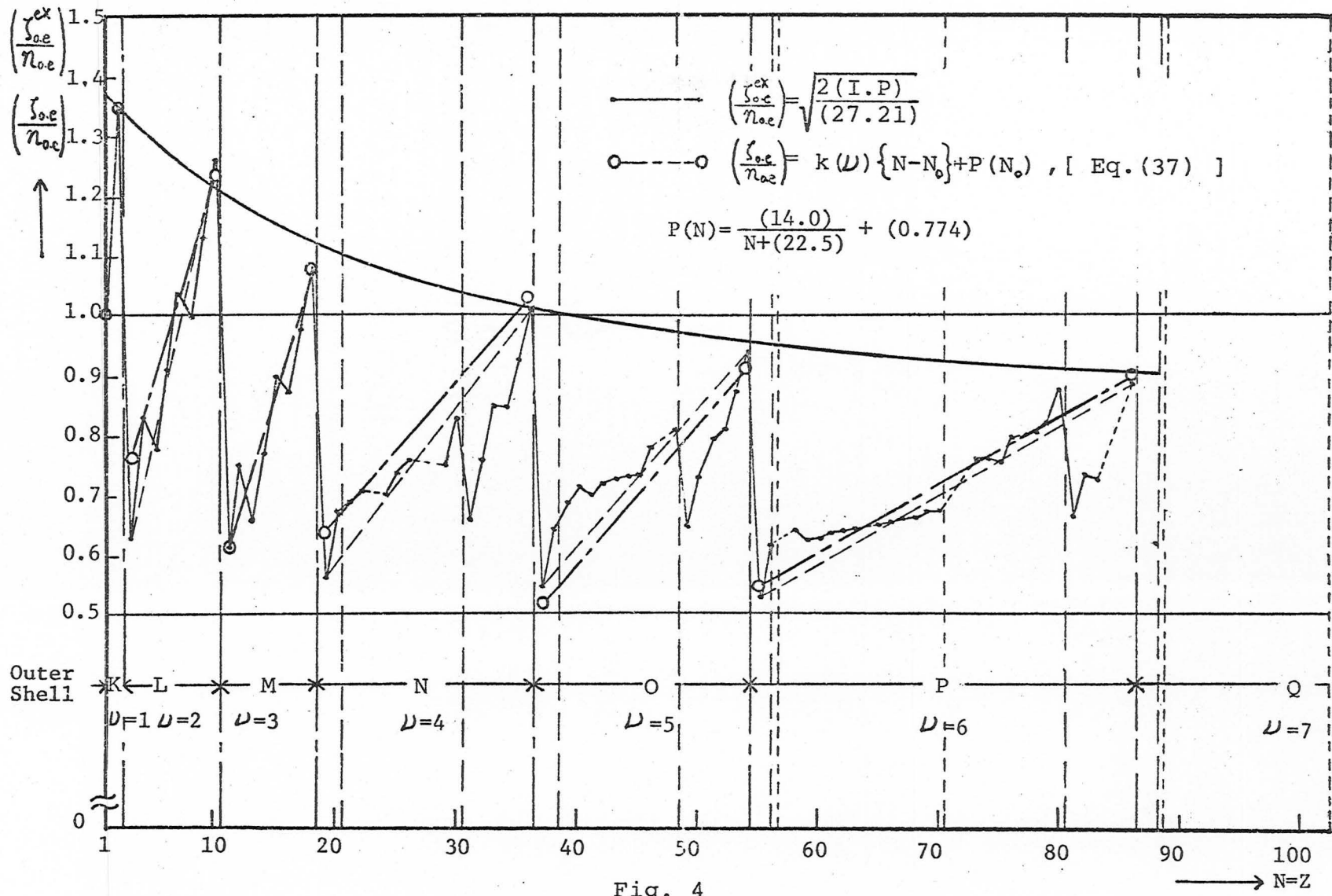


Fig. 4

2-4. Group Theoretical Implications of the Effective Nuclear Charge and an Idea for the Classification of Chemical Elements

Both expressions of  $\zeta$  given in sections 2-2 and 2-3 [Eqs. (27) and (37)] are not simple enough to obtain a useful dynamical group of the differential equation  $\left\{ \frac{p^2}{2} - \frac{(\zeta_{o.e})_{op}}{r} - i \frac{\partial}{\partial t} \right\} \psi_{o.e} = 0$ . But we will still see some group theoretical meanings in the expression of the effective nuclear charge  $\zeta$ . We notice the expression given in section 2-3 [Eq. (37)] is more convenient than Eq. (27) for our purpose, because Eq. (37) works in a wide range of atomic numbers and it has important characteristics of the periodic chart. Now we will think about some meanings of  $\zeta$  mainly for Eq. (37).

Let the third quantized Hamiltonian, and energy for an outer electron be approximately given as\*

$$H_{o.e} = \frac{p^2}{2} - \frac{(\zeta_{o.e})_{op}}{r}, \quad E_{o.e} = -\frac{1}{2} \left( \frac{\zeta_{o.e}}{n_{o.e}} \right)^2, \quad (38)$$

with a third quantized wavefunction  $\psi'_{o.e} = f_{o.e}(s) \phi_{o.e}(F)$ . Let  $\zeta_{o.e}$  be given by Eq. (37):

---

\* See section 2-1.  
The definition of outer electrons is given in section 2-3; p. 25.

$$\left(\frac{J_{o.e}}{n_{o.e}}\right) = \frac{(0.496)}{\nu\{\nu+(-1)^\nu\} + (1.442)} \left\{ Z - 0.17(\nu+2)^3 + \{1.9 + 0.7(-1)^{\nu+1}\} \right\} \\ + \frac{(14.0)}{0.17(\nu+2)^3 - \{1.9 + 0.7(-1)^{\nu+1}\} + 22.5} + (0.774) \quad (37)$$

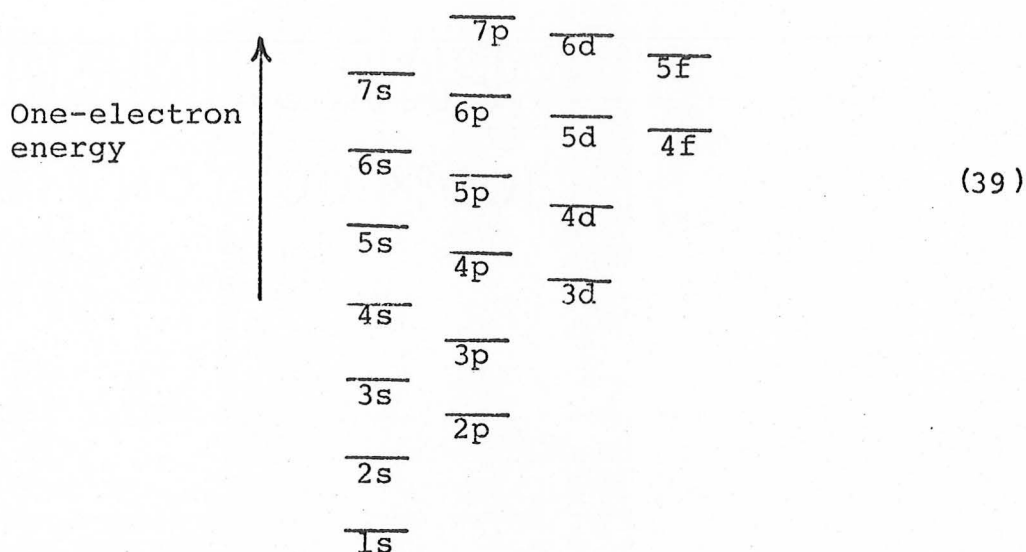
The degeneracy group of the outer electron is generated by generators  $Q(r, s, \ell, \frac{\partial}{\partial r}, \frac{\partial}{\partial s}, \frac{\partial}{\partial \ell}, \dots)$  which satisfy the equation  $(H_{o.e} - E_{o.e}) Q \psi'_{o.e} = 0$  under the condition of  $(H_{o.e} - E_{o.e}) \psi'_{o.e} = 0$ .\* The generators  $Q$  will in this case include the quantity  $E_{o.e}$  in their expressions, therefore the eigenvalues of the Casimir operators of the degeneracy group will be functions of  $\nu$  and  $Z$  in our approximation by Eq. (37). Looking at Eq. (37) we see the quantities  $\nu\{\nu+(-1)^\nu\}$  and  $\nu$  determine the main characteristics of the periodic chart. This suggests the above degeneracy group has subgroups determined by these two numbers and so does the dynamical group mentioned in section 2-1. Consequently we may say the classification group<sup>+</sup> of the periodic chart has subgroups determined by the labeling numbers  $\nu\{\nu+(-1)^\nu\}$  and  $\nu$ .

---

\* The operators of this degeneracy group permit us to change an outer electron state of any ground state atom to a degenerate outer electron state of another ground state atom. In other word these operators allow us to pass from a point of the lines  $\circ \text{---} \text{---} \circ$  in Fig.4. to another point of the same energy level on these lines. See p.12-13.

+ Here classification group means a group whose single UIR (unitary irreducible representation) labels and classify all the chemical elements well describing the characteristics of the chart.

Now let us construct a good group theoretical labeling scheme that characterizes and classifies chemical elements using these two numbers. To begin with, it will be a good idea to think about the well known Aufbau scheme<sup>(6,9)</sup> which gives an ordering of one-electron energy levels for many-electron atoms. Especially for outer electrons this scheme has quite good characteristics,\* and it is given as



Looking at the scheme we find the following approximate orbital degeneracy patterns: (2s,2p); (3s,3p); (4s,4p,3d); (5s,5p,4d); (6s,6p,5d,4f); (7s,7p,6d,5f);..... For the first approximation we might think there would exist the exact degeneracy pattern

---

\* Cf. Fig.3 (section 2-2).

$$\begin{array}{cccc}
 \nu=7 & \overline{7s} & \overline{7p} & \overline{6d} & \overline{5f} \\
 \nu=6 & \overline{6s} & \overline{6p} & \overline{5d} & \overline{4f} \\
 \nu=5 & \overline{5s} & \overline{5p} & \overline{4d} & \\
 \nu=4 & \overline{4s} & \overline{4p} & \overline{3d} & \\
 \nu=3 & \overline{3s} & \overline{3p} & & \\
 \nu=2 & \overline{2s} & \overline{2p} & & \\
 \nu=1 & \overline{1s} & & & 
 \end{array} \tag{40}$$

One finds each degenerate level can be labeled by the number  $\nu = n + l + \delta_{l,0} - 1$ . We notice this approximation is taken into account in Eq. (37) and is desirable for our discussion. Also notice the scheme of (40) has some similarities to the hydrogenic orbital degeneracy pattern

$$\begin{array}{cccc}
 n=4 & \overline{4s} & \overline{4p} & \overline{4d} & \overline{4f} \\
 n=3 & \overline{3s} & \overline{3p} & \overline{3d} & \\
 n=2 & \overline{2s} & \overline{2p} & & \\
 n=1 & \overline{1s} & & & 
 \end{array} \tag{41}$$

where each set of degenerate states provide a basis set of  $SO(4)$  unitary irreducible representation (UIR). This fact suggests each degenerate state of (40) can also provide a basis of an  $SO(4)$  UIR. If this is true, we have to say that each  $SO(4)$  UIR except the first appears twice because the

same degeneracy pattern repeats twice, except in the case of 1s. (e.g.  $\nu=2$  and  $\nu=3$ ,  $\nu=4$  and  $\nu=5$ ,  $\nu=6$  and  $\nu=7$ ,...)

Now let us think of the quantity  $\mu(\nu) = \nu\{\nu + (-1)^\nu\}$  which satisfies the relations  $\mu(2) = \mu(3)$ ,  $\mu(4) = \mu(5)$ ,  $\mu(6) = \mu(7)$ , .... Using this relation we can construct the labeling numbers of SO(4) for the scheme (40) as  $P = \mathcal{N}(\nu) - 1$ ,  $Q = 0^*$

where

$$\mathcal{N}(\nu) = \frac{1}{4} \left[ 3 + \sqrt{1 + 4\nu\{\nu + (-1)^\nu\}} \right]. \quad (42)$$

$\nu$	1	2	3	4	5	6	7	8	9	...
$\mu(\nu)$	0	6	20	42	72	...				
$\mathcal{N}(\nu)$	1	2	3	4	5	...				

The degeneracy pattern of (40) will be characterized by two numbers  $\nu$  and  $\mathcal{N}(\nu)$  as

---

\* The SO(4) is isomorphic to SU(2) x SU(2), and the eigenvalues of the Casimir operators of these SU(2)s are written as  $J_a^2 = J_a(J_a + 1)$ ,  $J_b^2 = J_b(J_b + 1)$ . The P and Q are defined as  $P = J_a + J_b$ ,  $Q = J_a - J_b$ . In order to have the pattern of (43), Q must be equal to zero:  $J_a = J_b$ .



$$\begin{array}{l}
\mathcal{N}(\nu) = 4 \quad \left\{ \begin{array}{l} \nu = 7 \\ \nu = 6 \end{array} \right. \quad \begin{array}{c} \overline{7s} \quad \overline{7p} \quad \overline{6d} \quad \overline{5f} \\ \overline{6s} \quad \overline{6p} \quad \overline{5d} \quad \overline{4f} \end{array} \\
\mathcal{N}(\nu) = 3 \quad \left\{ \begin{array}{l} \nu = 5 \\ \nu = 4 \end{array} \right. \quad \begin{array}{c} \overline{5s} \quad \overline{5p} \quad \overline{4d} \\ \overline{4s} \quad \overline{4p} \quad \overline{3d} \end{array} \\
\mathcal{N}(\nu) = 2 \quad \left\{ \begin{array}{l} \nu = 3 \\ \nu = 2 \end{array} \right. \quad \begin{array}{c} \overline{3s} \quad \overline{3p} \\ \overline{2s} \quad \overline{2p} \end{array} \\
\mathcal{N}(\nu) = 1 \quad \nu = 1 \quad \overline{1s}
\end{array} \tag{43}$$

and we notice that Eq.(37) espouses this classification.

Now we would like to obtain a classification group whose single UIR admits every state labeled by  $\nu$  and  $\mathcal{N}(\nu)$ , therefore this representation must contain two different SO(4) UIRs for each number  $\mathcal{N}(\nu) \geq 2$  and only one SO(4) UIR for  $\mathcal{N}(1) = 1$ . It is clear that we have to think about larger groups than SO(4). First we may think about SO(4) x SO(4), SO(4,1), SO(4,2), but none of them can be our classification group because of the following facts.

Since SO(4) is simply reducible, the representation  $(pq) \times (p'q')$  of SO(4) x SO(4) reduced to SO(4) contains every UIR of SO(4) labeled by P and Q either once or not at all,<sup>(35)</sup> therefore it cannot explain the doubling of SO(4) for each number of  $\mathcal{N}(\nu) \geq 2$ . The basis of the single UIR of SO(4,2) that contains all the hydrogenic functions, is also a basis

for a UIR of  $SO(4,1)$ .<sup>(36)</sup> It is known that there is no UIR of  $SO(4,1)$  that contains a given representation of  $SO(4)$  more than once.<sup>(37)</sup> Consequently this representation does not allow the doubling of  $SO(4)$  representations which seems to appear in the Aufbau chart. That is, there exists no unitary transformation in the space of these hydrogenic functions which can give rise to a new set of functions which have two subsets with the same  $SO(4)$  symmetry properties.

From other investigations being carried on here at University of the Pacific, it appears that one of the pseudo orthogonal groups  $SO(p,q)$  with  $p+q > 6$  may be usable as a dynamical group of Kepler systems whose charge  $Z$  is a dynamical variable.<sup>(38)</sup> Hence we naturally ask, is there such a group which has UIR that contains a one-dimensional  $SO(4)$  UIR just once and contains all other  $SO(4)$  UIR just twice?

Let us suppose that the one-electron SCF wave functions appropriate to the Aufbau chart are well approximated by finite linear combinations of hydrogenic functions with quantum numbers  $Z, n, \ell, m$ . Then if  $SO(p,q)$  is a dynamical group of the hydrogenic systems with variable  $Z$ ,  $SO(p+q)$  should provide an approximate dynamical group whose UIR can contain all hydrogenic functions up to some finite limiting values of  $Z, n, \ell, m$ .<sup>(39)</sup> We are then led to ask if there is an orthogonal group  $SO(n)$  which has a single UIR containing the requisite  $SO(4)$  UIRs. As it may easily be shown that a single

UIR of  $SO(6)$  can not contain the required  $SO(4)$  UIR,\* we proceed to a consideration of  $SO(7)$ .

The irreducible representations of  $SO(7)$  are determined by three labeling numbers  $m_{71}$ ,  $m_{72}$  and  $m_{73}$ .<sup>+</sup> The standard generators  $A_{ij}$  ( $1 \leq i \leq j \leq 7$ ) obey the commutation relations

$$[A_{ij}, A_{kl}] = \delta_{jk} A_{il} + \delta_{il} A_{jk} - \delta_{ik} A_{jl} - \delta_{jl} A_{ik}, \quad (44)$$

and they are antihermitian.

$$A_{ij} = -A_{ij}^{\dagger} \quad (45)$$

The vectors in the representation space are completely labeled in a group chain

$$SO(7) \supset SO(6) \supset SO(5) \supset SO(4) \supset SO(3) \supset SO(2). \quad (46)$$

we denote a vector in the representation space by  $|m_{ij}\rangle$ , where  $m_{ij}$  is an abbreviation for a complete set of labels.

---

\* The argument will be seen to be an obvious corollary of the  $SO(7)$  discussion which follows.

+ Here we use a discussion due to Gel'fand and Zetlin. (40)

$$|m_{ij}\rangle = \left| \begin{array}{ccc} m_{71} & m_{72} & m_{73} \\ m_{61} & m_{62} & m_{63} \\ m_{51} & m_{52} & \\ m_{41} & m_{42} & \\ m_{31} & & \\ m_{21} & & \end{array} \right. \quad (47)$$

The  $m_{7j}$ ,  $m_{6j}$ ,  $m_{5i}$ ,  $m_{4i}$ ,  $m_{31}$ ,  $m_{21}$  ( $j=1,2,3$ ;  $i=1,2$ ) are the labeling numbers of the  $SO(7)$ ,  $SO(6)$ ,  $SO(5)$ ,  $SO(4)$ ,  $SO(3)$ ,  $SO(2)$  UIRs respectively. All labels  $m_{ij}$  are integers and obey the conditions

$$|m_{61}| \leq m_{71} \leq m_{62} \leq m_{72} \leq m_{63} \leq m_{73}, \quad (48-a)$$

$$|m_{61}| \leq m_{51} \leq m_{62} \leq m_{52} \leq m_{63}, \quad (48-b)$$

$$|m_{41}| \leq m_{51} \leq m_{42} \leq m_{52}, \quad (48-c)$$

$$|m_{41}| \leq m_{31} \leq m_{42}, \quad (48-d)$$

$$|m_{21}| \leq m_{31}. \quad (48-e)$$

From the previous discussions and Eq.(48), we should say

$$m_{41} = Q = 0, \quad (49)$$

$$m_{42} = P = \mathcal{N}(\nu) - 1. \quad (50)$$

Eq.(49) means that the eigenvalue of the second second-

order Casimir operator is zero. If in a representation of the 5-dimensional orthogonal (pseudo-orthogonal) group the second second-order Casimir operator of any of the 5 (physically different) 4-dimensional orthogonal (pseudo-orthogonal) subgroups is zero, then the fourth-order Casimir operator of the 5-dimensional orthogonal (pseudo-orthogonal) group is zero.<sup>(41)</sup> Therefore we must have

$$m_{51}=0. \quad (41,42) \quad (51)$$

From Eqs. (48-b) and (51) we have to have

$$m_{61}=0. \quad (52)$$

Hence the vector in our representation space is labeled as

$$|m_{ij}\rangle = \begin{array}{cccc} & m_{71} & m_{72} & m_{73} \\ 0 & & m_{62} & m_{63} \\ & 0 & & m_{52} \\ 0 & & P & \\ & m_{31} & & \\ m_{21} & & & \end{array} \quad (53)$$

Here we have to notice again that our labeling scheme must allow the existence of just two different  $SO(4)$  UIRs for  $P \cong 1$  and only one  $SO(4)$  UIR for  $P = 0$ . In order to realize this fact by the group chain (46), we will have just two

different labeling schemes for each case  $P \geq 1$  and only one scheme for  $P = 0$ . For  $0 \leq P \leq P^0$  ( $P^0$  is a fixed number),\* we have two possible ways (54) and (55) to realize this fact by the group chain (46) with a single UIR of  $SO(7)$ :

$$|m_{ij}\rangle = \begin{array}{c} m_{71}^{(1)} \quad 1 \quad (P^0 + 1) \\ 0 \quad 1 \quad (P+1) \\ 0 \quad \quad \overline{m}_{52}^{(1)} \\ 0 \quad P \\ m_{31}^{\circ} \\ m_{21}^{\circ} \end{array} \quad (54)$$

$$|m_{ij}\rangle = \begin{array}{c} 0 \quad 1 \quad m_{73}^{(2)} \\ 0 \quad \overline{m}_{62}^{(2)} \quad P^0 \\ 0 \quad P \\ 0 \quad P \\ m_{31}^{\circ} \\ m_{21}^{\circ} \end{array} \quad (55)$$

In the scheme (54),  $m_{71}^{(1)}$  is a fixed number which is 0 or 1. The  $\overline{m}_{52}^{(1)}$  can just take values  $P$  or  $(P+1)$  for  $P \geq 1$ , but it can only take the value  $(P+1)=1$  for  $P=0$ , because we have the

---

\* When we have  $P^0 \geq 3$ , our schemes cover all the states of outer electrons in atomic ground states which appear in the periodic chart.

following relations from Eqs. (48-b,c):

$$P \leq \overline{m}_{52}^{(1)} \leq P+1, \quad (56)$$

$$1 \leq \overline{m}_{52}^{(1)}. \quad (57)$$

In the scheme (55),  $m_{73}^{(2)}$  is a fixed number which is greater than or equal to  $P^0$ . The  $\overline{m}_{62}^{(2)}$  can just take values 0 or 1 for  $P \geq 1$ , but it can only be zero for  $P=0$ , because of the relation

$$0 \leq \overline{m}_{62}^{(2)} \leq 1, \quad (58)$$

$$\overline{m}_{62}^{(2)} \leq P, \quad (59)$$

which is obvious from Eqs. (48-a,b).

Here we notice the  $\overline{m}_{52}^{(1)}$  and  $\overline{m}_{62}^{(2)}$  are written by using the numbers  $\nu$  and  $\mathcal{N}(\nu)$ :

$$\overline{m}_{52}^{(1)} = \nu - \mathcal{N}(\nu) + 1, \quad (60)$$

$$\overline{m}_{62}^{(2)} = 2\mathcal{N}(\nu) - \nu - 1. \quad (61)$$

$\mathcal{N}(\nu)$	1	2	3	4	5	.....				
$\nu$	1	2	3	4	5	6	7	8	9	.....
$\overline{m}_{52}^{(1)} = \nu - \mathcal{N}(\nu) + 1$	1	1	2	2	3	3	4	4	5	.....
$\overline{m}_{62}^{(2)} = 2\mathcal{N}(\nu) - \nu - 1$	0	1	0	1	0	1	0	1	0	.....

(62)

In both schemes the  $m_{31}^{\circ}$  and  $m_{21}^{\circ}$  are some fixed numbers which will be determined by the further classification within a state designated by  $\nu$ .

As we mentioned in section 2-1, the group structure of the periodic chart is determined by the group structure of the outer electron levels in atomic ground states, therefore chemical elements should be classified by a labeling scheme for an Aufbau chart. Remembering that in the periodic chart the s, p, d and f outer electrons appear in the series of  $I_a$ - $II_a$  typical elements,  $III_b \sim 0$  (rare gas) typical elements, transition elements and inner transition elements respectively, we notice that the  $m_{31}$  should rather be used for the classification of this kind than for the azimuthal quantum number of the outer electron, and in this sense we write  $m_{31} = \lambda$ . Our classification by the numbers  $\nu$ ,  $\mathcal{N}(\nu)$  and  $\lambda$  is shown in Fig.5. The  $m_{21}$  will further classify the elements in some way and we call it  $\mu$ . Now our labeling scheme will be

$$|m_{ij}\rangle = \begin{array}{c} \left. \begin{array}{ccc} m_{71}^{(1)} & 1 & \mathcal{N}^{\circ} \\ 0 & 1 & \mathcal{N}(\nu) \\ 0 & [\nu - \mathcal{N}(\nu) + 1] & \\ 0 & [\mathcal{N}(\nu) - 1] & \end{array} \right\} \\ \mu \quad \lambda \end{array} \quad (63)$$



or

$$|m_{ij}\rangle = \begin{pmatrix} 0 & 1 & m_{73}^{(2)} \\ 0 & [2\mathcal{N}(\omega) - \nu - 1] & [\mathcal{N}^{\circ} - 1] \\ 0 & 0 & [\mathcal{N}(\omega) - 1] \\ 0 & [\mathcal{N}(\omega) - 1] & \\ \lambda & & \\ \mu & & \end{pmatrix} \quad (64)$$

$$(\mathcal{N}^{\circ} \equiv P^{\circ} + 1)$$

Both schemes tell us that the  $SO(7)$  will be the smallest orthogonal group with a single UIR that contains the  $SO(4)$  UIR that seem to be required for the periodic chart. Thus we expect that the  $SO(p,q)$  with  $p+q=7$ ,  $p \geq 4$  will be an approximate subgroup of the classification group of all the states of all the chemical elements.

We have seen from Eq. (37) and (27) that the actual nuclear charge  $Z$  is also an important number together with  $\nu$  and  $\mathcal{N}(\nu)$  for the group theoretical classification. Noticing that  $Z$  should be expressed as a function of  $\nu, \lambda, \mu$  and some other labeling number(s)  $\square$  as

$$Z = (\nu, \lambda, \mu; \square), \quad (65)$$

we know that the vector in the representation space of our

complete classification group\* may be labeled by the numbers  $\nu, \lambda, \mu$  and  $\square$ , and this group may have a noncompact 7-dimensional subgroup whose representation space is spanned by the vectors labeled by  $\nu, \lambda$  and  $\mu$ .

---

\* Our complete classification group will be a subgroup of a group obtained by Eq. (9) in section 2-1.

	$\lambda = 0$	$\lambda = 1$	$\lambda = 2$	$\lambda = 3$	
$N(\omega)=4$	$\nu=7$	Fr Ra 87 88		Lr Ku 103 104	Ac Th Pa U Np Pu Am Cm Bk Cf E Fm Md No 89 90 91 92 93 94 95 96 97 98 99 100 101 102
	$\nu=6$	Cs Ba 55 56	Tl Pb Bi Po At Rn 81 82 83 84 85 86	Lu Hf Ta W Re Os Ir Pt Au Hg 71 72 73 74 75 76 77 78 79 80	La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb 57 58 59 60 61 62 63 64 65 66 67 68 69 70
$N(\omega)=3$	$\nu=5$	Rb Sr 37 38	In Sn Sb Te I Xe 49 50 51 52 53 54	Y Zr Nb Mo Tc Ru Rh Pd Ag Cd 39 40 41 42 43 44 45 46 47 48	
	$\nu=4$	K Ca 19 20	Ga Ge As Se Br Kr 31 32 33 34 35 36	Sc Ti V Cr Mn Fe Co Ni Cu Zn 21 22 23 24 25 26 27 28 29 30	
$N(\omega)=2$	$\nu=3$	Na Mg 11 12	Al Si P S Cl Ar 13 14 15 16 17 18		
	$\nu=2$	Li Be 3 4	B C N O F Ne 5 6 7 8 9 10		
$N(\omega)=1$	$\nu=1$	H He 1 2			

Fig. 5

### III. A Group Theoretical Study of Configuration Mixing for the Ground State of Helium

In this chapter we try to investigate the manner in which symmetries of the one-electron problem are affected by the interaction between two electrons. We will examine the configuration mixing due to the  $1/r_{12}$  electron repulsion potential by reducing  $SO(4,1) \times SO(4,1)$  to an  $SO(4,1)$  in several ways. In section 3-1, a physical realization of the  $SO(4,2)$  algebra and the matrix representations of the generators will be given. We will elaborate the idea of our investigation in section 3-2, and the examination of the idea will be given in section 3-3 for the ground state of the helium atom.

### 3-1 A Physical Realization of the SO(4,2) Algebra

The generators of the dynamical group SO(4,2) admit many realizations. In series of papers (43,44,45) it was shown that these generators can be realized with the help of differential operators in the real variables  $x_1, x_2, x_3$ . For the treatment of a physical system, the following generators provide a convenient realization, because they are expressed by dynamical variables of the system in a particularly simple way. Using Bednář's notation<sup>(45)</sup> the generators are written as\*

$$L_k = -i \epsilon_{ijk} \left( x_i \frac{\partial}{\partial x_j} - x_j \frac{\partial}{\partial x_i} \right), \quad (1)$$

$$A_k = -\frac{1}{2} \left( x_k \nabla^2 - 2 \frac{\partial}{\partial x_k} - 2 x_j \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_k} + x_k \right), \quad (2)$$

$$B_k = -\frac{1}{2} \left( x_k \nabla^2 - 2 \frac{\partial}{\partial x_k} - 2 x_j \frac{\partial}{\partial x_j} \frac{\partial}{\partial x_k} - x_k \right), \quad (3)$$

$$T_1 = -\frac{1}{2} (r \nabla^2 + r), \quad (4)$$

$$T_2 = -i \left( x_j \frac{\partial}{\partial x_j} + 1 \right) = -i \left( r \frac{\partial}{\partial r} + 1 \right), \quad (5)$$

$$T_3 = -\frac{1}{2} (r \nabla^2 - r), \quad (6)$$

$$\Gamma_k = -i r \frac{\partial}{\partial x_k}, \quad (7)$$

where  $\nabla^2 = \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_i}$ ,  $r = (x_j x_j)^{1/2}$ ;  $k, i, j = 1, 2, 3$ .

---

\* Here a summation convention is used.

The commutation relations of these generators are:

	L	A	B	T	$\Gamma$
L	(a)	(f)	(j)	(m)	(o)
A		(b)	(g)	(k)	(n)
B			(c)	(h)	(l)
T				(d)	(i)
$\Gamma$					(e)

$$(a) [L_i, L_j] = i \epsilon_{ijk} L_k$$

$$(b) [A_i, A_j] = i \epsilon_{ijk} L_k$$

$$(c) [B_i, B_j] = -i \epsilon_{ijk} L_k$$

$$(d) [T_1, T_2] = -i T_3$$

$$[T_2, T_3] = i T_1$$

$$[T_3, T_1] = i T_2$$

$$[T_i, T_i] = 0$$

$$(e) [\Gamma_i, \Gamma_j] = -i \epsilon_{ijk} L_k$$

$$(f) [L_i, A_j] = i \epsilon_{ijk} A_k$$

$$(g) [A_i, B_j] = i \delta_{ij} T_2$$

$$(h) [B_i, T_1] = 0$$

$$[B_i, T_2] = -i A_i$$

$$[B_i, T_3] = i \Gamma_i$$

$$(i) [T_1, \Gamma_j] = i A_j$$

$$[T_2, \Gamma_j] = 0$$

$$[T_3, \Gamma_j] = i B_j$$

$$(j) [L_i, B_j] = i \epsilon_{ijk} B_k$$

$$(k) [A_i, T_1] = -i \Gamma_i$$

$$[A_i, T_2] = -i B_i$$

$$[A_i, T_3] = 0$$

$$(l) [B_i, \Gamma_j] = i \delta_{ij} T_3$$

$$(m) [L_i, T_j] = 0$$

$$(n) [A_i, \Gamma_j] = i \delta_{ij} T_1$$

$$(o) [L_i, \Gamma_j] = i \epsilon_{ijk} \Gamma_k$$

These generators act in the space of functions  $f(\vec{r})$ , and the scalar product of the functions is defined by

$\langle f, g \rangle = \int f^*(\vec{r}) g(\vec{r}) \cdot r d\vec{r}$  \*, so that the generators  $L, A, B, T, \Gamma$  are self-adjoint operators: (43)

$$\langle f, A_k g \rangle = \langle A_k f, g \rangle \text{ etc.} \quad (8)$$

Two sets of operators  $(L, A, B, T_2)$  and  $(L, A, \Gamma, T_1)$  generate two different subgroups  $SO(4,1)$ , and the generators  $L, A$  form an  $SO(4)$  subalgebra. The operators  $L$  and  $T$  form subalgebras  $SO(3)$  and  $SO(2,1)$  respectively.

From Eqs. (1) and (2) we have the relation

$$L \cdot A = 0, \quad (9)$$

which means that the second second-order Casimir operator of the subgroup  $SO(4)$  vanishes. Then the fourth-order Casimir operator of the  $SO(4,1)$  group also vanishes. (41) In the representation defined by (1)~(6), the second order Casimir operators of two different  $SO(4,1)$  groups and their eigenvalues are

$$(T_2)^2 + B^2 - L^2 - A^2 = 2, \quad (10)$$

$$(T_1)^2 + \Gamma^2 - L^2 - A^2 = 2. \quad (11)$$

---

\* Notice that the element of the space is  $r d\vec{r}$  instead of  $r^2 d\vec{r}$ .

Therefore the structure of the unitary irreducible representation space of the  $SO(4,1)$  group generated by  $(\mathbb{L}, \mathbb{A}, \mathbb{B}, T_2)$  or  $(\mathbb{L}, \mathbb{A}, \mathbb{T}, T_1)$  is given by<sup>(45)</sup>

$$\mathcal{R} = \sum_{n=1}^{\infty} \oplus \mathcal{R}_n, \quad (12)$$

where  $\mathcal{R}_n$  is the representation space of the subgroup  $SO(4)$ . The Casimir operators of this  $SO(4)$  group are in the space  $\mathcal{R}_n$  represented by

$$\mathbb{A}^2 + \mathbb{L}^2 = n^2 - 1, \quad (13)$$

$$\mathbb{A} \cdot \mathbb{L} = 0. \quad (14)$$

Therefore the basis of the representation space  $\mathcal{R}$  can be chosen by  $|n \ l \ m\rangle$ ,

where

$$n = 1, 2, 3, \dots, \infty,$$

$$l = 0, 1, 2, \dots, n-1,$$

$$m = -l, -l+1, \dots, l.$$

From Eqs. (1), (2) and (6), we have the relation

$$\mathbb{L}^2 + \mathbb{A}^2 + 1 = (T_3)^2. \quad (15)$$

Comparing (13) and (15) we have an operator identity

$$T_3 = n, \quad (16)$$



from which we can obtain the coordinate representation  $\chi_{n\ell m}^{(\vec{r})}$  of the state  $|n\ell m\rangle$  as a solution of the eigenequation

$$T_3 \chi_{n\ell m}^{(\vec{r})} = n \chi_{n\ell m}^{(\vec{r})}. \quad (17)$$

The function  $\chi_{n\ell m}^{(\vec{r})}$  can be expressed in spherical coordinates as

$$\chi_{n\ell m}^{(\vec{r})} = \frac{2}{(2\ell+1)! \sqrt{(n-\ell-1)!}} \sqrt{\frac{(n+\ell)!}{(2\ell+1)!}} \cdot e^{-r} \cdot (2r)^\ell \cdot F(-n+\ell+1, 2\ell+2; 2r) \cdot Y_{\ell m}^{(\omega)}, \quad (18)$$

where  $F(\alpha, \gamma; x)$  is the confluent hypergeometric function.

The orthogonality relation for  $\chi_{n\ell m}^{(\vec{r})}$  are

$$\iint \chi_{n\ell m}^{*\prime(\vec{r})} \frac{1}{r} \chi_{n\ell m}^{(\vec{r})} \cdot r^2 dr d\omega = \delta_{n'n} \delta_{\ell\ell'} \delta_{m'm}. \quad (19)$$

Noticing that the hydrogenic wavefunction is written as

$$\psi_{n\ell m}^{(Z\vec{r}/n)} = \frac{1}{(2\ell+1)!} \sqrt{\frac{(2Z)^3 (n+\ell)!}{n^{2n} 2n(n-\ell-1)!}} \cdot e^{-Zr/n} \left(\frac{2Zr}{n}\right)^\ell F(-n+\ell+1, 2\ell+2; \frac{2Zr}{n}) \cdot Y_{\ell m}^{(\omega)}, \quad (20)$$

we can easily find the relationship between  $\chi_{n\ell m}^{(\vec{r})}$  and

$\psi_{n\ell m}^{(Z\vec{r}/n)}$  :

$$\psi_{n\ell m}^{(Z\vec{r}/n)} = \frac{\sqrt{Z}}{n} \cdot e^{i\theta T_2} \chi_{n\ell m}^{(\vec{r})} \quad [\theta \equiv \ln(Z/n)], \quad (21)$$

because

$$e^{i\theta T_2} f(\vec{r}) = e^\theta f(e^\theta \vec{r}). \quad (22)$$

The matrix representation of the SO(4) algebra is well known in the representation space  $\mathcal{R}_n^{(4)}$ .

$$L_3 |n l m\rangle = m |n l m\rangle, \quad (23)$$

$$L_\pm |n l m\rangle = \sqrt{(l \mp m)(l+1 \pm m)} |n, l, m \pm 1\rangle, \quad (24)$$

$$L^2 |n l m\rangle = l(l+1) |n l m\rangle, \quad (25)$$

$$A_3 |n l m\rangle = a_+^{(3)}(n l m) |n, l+1, m\rangle + a_-^{(3)}(n l m) |n, l-1, m\rangle, \quad (26)$$

$$A_\pm |n l m\rangle = a_+^{(\pm)}(n l m) |n, l \pm 1, m \pm 1\rangle + a_-^{(\pm)}(n l m) |n, l-1, m \pm 1\rangle, \quad (27)$$

where

$$L_\pm = L_1 \pm i L_2, \quad A_\pm = A_1 \pm i A_2,$$

$$a_+^{(3)}(n l m) = \frac{\sqrt{(l+1)^2 - m^2}}{\sqrt{4(l+1)^2 - 1}} \sqrt{n^2 - (l+1)^2},$$

$$a_-^{(3)}(n l m) = \frac{\sqrt{l^2 - m^2}}{\sqrt{4l^2 - 1}} \sqrt{n^2 - l^2},$$

$$a_+^{(\pm)}(n l m) = \mp \frac{\sqrt{n^2 - (l+1)^2}}{\sqrt{4(l+1)^2 - 1}} \sqrt{(l+2 \pm m)(l+1 \pm m)},$$

$$a_-^{(\pm)}(n l m) = \pm \frac{\sqrt{n^2 - l^2}}{\sqrt{4l^2 - 1}} \sqrt{(l \mp m)(l-1 \mp m)}.$$

The radial  $SO(2,1)$  generators are represented by

$$T_3 |n\ell m\rangle = n |n\ell m\rangle, \quad (28)$$

$$T_{\pm} |n\ell m\rangle = \sqrt{(\ell+1 \pm n)(\pm n - \ell)} |n \pm 1, \ell, m\rangle; \quad (29)$$

$$(T_3^2 - T_1^2 - T_2^2) |n\ell m\rangle = \ell(\ell+1) |n\ell m\rangle, \quad (30)$$

where  $T_{\pm} = T_1 \pm iT_2$ .

Using the commutation relation  $[A_i, T_2] = -iB_i$ , we have

$$\begin{aligned} B_3 |n\ell m\rangle &= b_{++}^{(3)}(n\ell m) |n+1, \ell+1, m\rangle + b_{+-}^{(3)}(n\ell m) |n+1, \ell-1, m\rangle \\ &\quad + b_{-+}^{(3)}(n\ell m) |n-1, \ell+1, m\rangle + b_{--}^{(3)}(n\ell m) |n-1, \ell-1, m\rangle, \end{aligned} \quad (31)$$

$$\begin{aligned} B_{\pm} |n\ell m\rangle &= b_{++}^{(\pm)}(n\ell m) |n+1, \ell+1, m \pm 1\rangle + b_{+-}^{(\pm)}(n\ell m) |n+1, \ell-1, m \pm 1\rangle \\ &\quad + b_{-+}^{(\pm)}(n\ell m) |n-1, \ell+1, m \pm 1\rangle + b_{--}^{(\pm)}(n\ell m) |n-1, \ell-1, m \pm 1\rangle, \end{aligned} \quad (32)$$

where  $B_{\pm} = B_1 \pm iB_2$ ,

$$b_{++}^{(3)}(n\ell m) = \frac{1}{2} \sqrt{\frac{(\ell+1)^2 - m^2}{4(\ell+1)^2 - 1}} \sqrt{(n+\ell+1)(n+\ell+2)},$$

$$b_{+-}^{(3)}(n\ell m) = \frac{1}{2} \sqrt{\frac{\ell^2 - m^2}{4\ell^2 - 1}} \sqrt{(n-\ell)(n-\ell+1)},$$

$$b_{-+}^{(3)}(n\ell m) = \frac{1}{2} \sqrt{\frac{(\ell+1)^2 - m^2}{4(\ell+1)^2 - 1}} \sqrt{(n-\ell-1)(n-\ell-2)},$$

$$b_{--}^{(3)}(n\ell m) = \frac{1}{2} \sqrt{\frac{\ell^2 - m^2}{4\ell^2 - 1}} \sqrt{(n+\ell)(n+\ell-1)},$$

$$b_{++}^{(\pm)}(n\ell m) = \mp \frac{1}{2} \sqrt{\frac{(\ell+2\pm m)(\ell+1\pm m)}{4(\ell+1)^2-1}} \sqrt{(n+\ell+1)(n+\ell+2)},$$

$$b_{+-}^{(\pm)}(n\ell m) = \pm \frac{1}{2} \sqrt{\frac{(\ell\mp m)(\ell\mp m-1)}{4\ell^2-1}} \sqrt{(m-\ell)(m-\ell+1)},$$

$$b_{-+}^{(\pm)}(n\ell m) = \mp \frac{1}{2} \sqrt{\frac{(\ell+2\pm m)(\ell+1\pm m)}{4(\ell+1)^2-1}} \sqrt{(n-\ell-1)(n-\ell-2)},$$

$$b_{--}^{(\pm)}(n\ell m) = \pm \frac{1}{2} \sqrt{\frac{(\ell\mp m)(\ell\mp m-1)}{4\ell^2-1}} \sqrt{(n+\ell)(n+\ell-1)}.$$

Using the commutation relation  $[A_i, T_i] = -i\Gamma_i$ , we obtain

$$\begin{aligned} \Gamma_3 |n\ell m\rangle &= \gamma_{++}^{(3)}(n\ell m) |n+1, \ell+1, m\rangle + \gamma_{+-}^{(3)}(n\ell m) |n+1, \ell-1, m\rangle \\ &\quad + \gamma_{-+}^{(3)}(n\ell m) |n-1, \ell+1, m\rangle + \gamma_{--}^{(3)}(n\ell m) |n-1, \ell-1, m\rangle, \end{aligned} \quad (33)$$

$$\begin{aligned} \Gamma_{\pm} |n\ell m\rangle &= \gamma_{++}^{(\pm)}(n\ell m) |n+1, \ell+1, m\pm 1\rangle + \gamma_{+-}^{(\pm)}(n\ell m) |n+1, \ell-1, m\pm 1\rangle \\ &\quad + \gamma_{-+}^{(\pm)}(n\ell m) |n-1, \ell+1, m\pm 1\rangle + \gamma_{--}^{(\pm)}(n\ell m) |n-1, \ell-1, m\pm 1\rangle, \end{aligned} \quad (34)$$

where  $\Gamma_{\pm} = \Gamma_1 \pm i\Gamma_2$ ,

$$\gamma_{++}^{(3)}(n\ell m) = \frac{i}{2} \sqrt{\frac{(\ell+1)^2-m^2}{4(\ell+1)^2-1}} \sqrt{(n+\ell+1)(n+\ell+2)},$$

$$\gamma_{+-}^{(3)}(n\ell m) = \frac{i}{2} \sqrt{\frac{\ell^2-m^2}{4\ell^2-1}} \sqrt{(m-\ell)(m-\ell+1)},$$

$$\gamma_{-+}^{(3)}(n\ell m) = \frac{-i}{2} \sqrt{\frac{(\ell+1)^2-m^2}{4(\ell+1)^2-1}} \sqrt{(n-\ell-1)(n-\ell-2)},$$

$$\gamma_{--}^{(3)}(n\ell m) = \frac{-i}{2} \sqrt{\frac{\ell^2-m^2}{4\ell^2-1}} \sqrt{(n+\ell)(n+\ell-1)},$$

$$y_{++}^{(\pm)}(n\ell m) = \mp \frac{i}{2} \sqrt{\frac{(\ell+2\pm m)(\ell+1\pm m)}{4(\ell+1)^2-1}} \sqrt{(n+\ell+1)(n+\ell+2)},$$

$$y_{+-}^{(\pm)}(n\ell m) = \pm \frac{i}{2} \sqrt{\frac{(\ell\mp m)(\ell-1\mp m)}{4\ell^2-1}} \sqrt{(n-\ell)(n-\ell+1)},$$

$$y_{-+}^{(\pm)}(n\ell m) = \pm \frac{i}{2} \sqrt{\frac{(\ell+2\pm m)(\ell+1\pm m)}{4(\ell+1)^2-1}} \sqrt{(n-\ell-1)(n-\ell-2)},$$

$$y_{--}^{(\pm)}(n\ell m) = \mp \frac{i}{2} \sqrt{\frac{(\ell\mp m)(\ell-1\mp m)}{4\ell^2-1}} \sqrt{(n+\ell)(n+\ell-1)},$$

We can also find the explicit matrix representations of the operators  $\vec{T}$  and  $r$ , because of the relations

$$\vec{T} = \mathbb{B} - \mathbb{A}, \quad (35)$$

$$r = T_3 - T_1, \quad (36)$$

which are obvious from Eqs. (2), (3) and (4), (6).

3-2. On an Approximate Dynamical Symmetry  
of the Helium Atom

It is well known that the symmetry group of the Hamiltonian of the hydrogen atom is the four-dimensional orthogonal group  $SO(4)$ .<sup>(46)</sup>

In this chapter our purpose will be to investigate the manner in which symmetries of the one-electron problem are affected by the interaction between two electrons. Obviously a fundamental task is to study the effect on dynamical symmetry of  $1/r_{12}$ , the electron repulsion potential. The matrix elements of the  $1/r_{12}$  potential were examined by Kumei and Wulfman in terms of those of the generators of  $SO(4,2)$ .<sup>(28)</sup> Wulfman found that the configuration mixing in complexes of definite  $n_1, n_2 = n_1^*$ , which is due to the  $1/r_{12}$  term in the Hamiltonian, may be such as to nearly diagonalize  ${}^{12}\mathbf{A} \cdot {}^{12}\mathbf{A}$ , where  ${}^{12}\mathbf{A} = {}^1\mathbf{A} - {}^2\mathbf{A}$ ,  ${}^i\mathbf{A}$  being the Hamilton-Runge-Lenz vector<sup>+</sup> of particle  $i$ .<sup>(29)</sup> In order to predict the form of such a mixing, he reduced  $SO(4) \times SO(4)$  to  $SO(4)$  in the following way.<sup>(29)</sup>

---

\* The  $n_1$  and  $n_2$  are the radial quantum numbers of electrons 1 and 2.

+ The Hamilton-Runge-Lenz vector has a form of Eq.(2) in a representation space defined by section 3-1.

Consider the pseudospin operators<sup>(47)</sup> of particle  $i$ , viz.,  ${}^iM = \frac{1}{2}({}^iL + {}^iA)$  and  ${}^iN = \frac{1}{2}({}^iL - {}^iA)$ , where  ${}^iL$  is the angular momentum operator of particle  $i$ . Couple  ${}^1M$  with  ${}^2N$  to get  $J_a$ , and couple  ${}^1N$  with  ${}^2M$  to get  $J_b$ . Couple  $J_a$  with  $J_b$  to get  ${}^2L = {}^1L + {}^2L$ . Denote the resulting two-electron functions  $|(n_1 n_2) P Q L M\rangle$ , where  $P = J_a + J_b$ , and  $Q = J_a - J_b$ ;  $J_a(J_a + 1)$  and  $J_b(J_b + 1)$  being eigenvalues of  $J_a^2$  and  $J_b^2$ . These functions are eigenfunctions of  $({}^1A)^2 + ({}^1L)^2 + 1$ ,  $({}^2A)^2 + ({}^2L)^2 + 1$ ,  $({}^{12}A)^2 + ({}^{12}L)^2$ ,  $({}^{12}A \cdot {}^{12}L)^2$ ,  $({}^{12}L)^2$ ,  $({}^{12}L)_z$ , with eigenvalues respectively of  $n_1^2$ ,  $n_2^2$ ,  $P(P+2) + Q^2$ ,  $\{Q(P+1)\}^2$ ,  $L(L+1)$ ,  $M$ . The functions obtained in this way are related to those of the usual basis  $\psi_{LM}^{n_1 l_1 n_2 l_2}$  by the recoupling transformation\*

$$|(n_1 n_2) P Q L M\rangle = - \sum_{l_1 l_2} (-1)^{l_2 - n_2} [(2l_1 + 1)(2l_2 + 1)(P + Q + 1)(P - Q + 1)]^{\frac{1}{2}} \begin{Bmatrix} \frac{1}{2}(n_1 - 1) & \frac{1}{2}(n_1 - 1) & l_1 \\ \frac{1}{2}(n_2 - 1) & \frac{1}{2}(n_2 - 1) & l_2 \\ \frac{1}{2}(P + Q) & \frac{1}{2}(P - Q) & L \end{Bmatrix} \psi_{LM}^{n_1 l_1 n_2 l_2} \quad (37)$$

When the mixing with definite  $n_1 = n_2$  is possible, Eq. (37) "fixes the mix". For the doubly excited states of helium, this equation gives quite good agreement with the results obtained by diagonalizing  $1/r_{12}$  using the bases of definite  $n_1 = n_2$ .

---

\* For the detailed discussion, see Ref. (29).

The expectation value of the  $1/r_{12}$  potential for the state  $|(n^n)PQLM\rangle$  may be given approximately by<sup>(29)</sup>

$$V \approx n^{-1} \left\{ P(P+2) + Q^2 - L(L+1) + n^2 + 2 + \frac{1}{2} \langle 1^{(1L)^2} + 1^{(2L)^2} | \rangle \right\}^{-\frac{1}{2}} \quad (38)$$

The eigenvalue of  ${}^{12}A \cdot {}^{12}A$  is  $P(P+2) + Q^2 - L(L+1)$ . This is the dominant factor in the  $1/r_{12}$  potential, and it is the reason why the proper mixing for the doubly excited states of He is given by  $|(n^n)PQLM\rangle$  which is the basis vector of the group  $SO(4)$  generated by  ${}^{12}A = {}^1A - {}^2A$  and  ${}^{12}L = {}^1L + {}^2L$ . Unfortunately we cannot obtain a higher approximation to the ground state of the helium atom or to its singly excited states, because the generators of  $SO(4)$  do not allow us to change the radial quantum numbers of one-electron states as we saw in Eqs. (23)~(27) in the previous section.

In order to have more general configuration mixings, it is clear that we have to think about the superposition of numbers of different states labeled by  $n_1$  and  $n_2$ . We would like to predict the proper mixing without doing the usual diagonalization of the Hamiltonian matrix. From Eqs. (23)~(34) in the previous section, we know that the generators of  $SO(4,1)$  can change the radial quantum numbers operating on state vectors, therefore we might expect that we could get a proper configuration mixing by the aid of the reduction of



SO(4,1) x SO(4,1) to an SO(4,1). The following sets of operators generate such SO(4,1) groups\* :

$$(i) \quad {}^2L = {}^1L + {}^2L, \quad {}^2A = {}^1A - {}^2A, \quad {}^2B = {}^1B - {}^2B, \quad {}^2T_2 = {}^1T_2 + {}^2T_2$$

$$(ii) \quad {}^2L = {}^1L + {}^2L, \quad {}^2A = {}^1A - {}^2A, \quad {}^2B = {}^1B + {}^2B, \quad {}^2T_2 = {}^1T_2 - {}^2T_2$$

$$(iii) \quad {}^2L = {}^1L + {}^2L, \quad {}^2A = {}^1A - {}^2A, \quad {}^2T = {}^1T - {}^2T, \quad {}^2T_1 = {}^1T_1 + {}^2T_1$$

$$(iv) \quad {}^2L = {}^1L + {}^2L, \quad {}^2A = {}^1A - {}^2A, \quad {}^2T = {}^1T + {}^2T, \quad {}^2T_1 = {}^1T_1 - {}^2T_1$$

The basis vectors  $|RSPQLM\rangle$  of these two-particle SO(4,1) groups will be written as a linear combination of the two-particle SO(4) basis vectors  $|(n_1' n_2')PQLM\rangle$  :

$$|RSPQLM\rangle = \sum_{n_1' n_2'} C_{n_1' n_2'}^{RS} |(n_1' n_2')PQLM\rangle, \quad (39)$$

where R and S are labeling numbers of the SO(4,1) group and we can require

$$\sum_{n_1 n_2} (C_{n_1 n_2}^{RS})^* (C_{n_1 n_2}^{RS}) = 1. \quad (40)$$

As we see in Eq.(39), the state  $|RSPQLM\rangle$  is described as a superposition of the states labeled by  $n_1'$  and  $n_2'$ .

---

\* By the study of doubly excited states of helium, we know  ${}^2L = {}^1L + {}^2L$  and  ${}^2A = {}^1A - {}^2A$  are physically important. Therefore we eliminate from considerations groups with generators  ${}^2L = {}^1L - {}^2L$  and  ${}^2A = {}^1A + {}^2A$ .

Now let us think about a reasonable way to get a proper configuration mixing. When we divide the Hamiltonian of the system by  $Z^2$  in the manner of the  $1/Z$ -expansion method, (18) we have

$$\mathcal{H} \equiv Z^{-2} H = \sum_{i=1}^2 \left( \frac{p_i^2}{2} - \frac{1}{s_i} \right) + \frac{1}{Z} \frac{1}{s_{12}}, \quad (41)$$

where  $s_i = Z r_i$ ,  $p_i = \frac{1}{Z} (-i) \nabla_i$ , and  $Z$  is the nuclear charge. The hydrogenic part  $\sum_{i=1}^2 (p_i^2/2 - 1/s_i)$  has an  $SO(4) \times SO(4)$  symmetry and it can be written as (47)\*

$$\sum_{i=1}^2 \left( \frac{p_i^2}{2} - \frac{1}{s_i} \right) = -\frac{1}{2} \sum_{i=1}^2 \left\{ ({}^i A)^2 + ({}^i L)^2 + 1 \right\}^{-1}. \quad (42)$$

Considering the previous discussion, we might ask whether the mixed configuration due to the  $1/s_{12}$  potential is an approximate eigenstate of  $|RSPQLM\rangle$ . We also notice that the ratio of the hydrogenic part and the electron repulsion part depends on  $Z$ , and the electron repulsion part must vanish when  $Z$  goes to infinity. Hence we might expect that the electronic state of helium may be approximated as a linear combination of the properly dilated states of  $|(n_1, n_2)PQLM\rangle$  and  $|RSPQLM\rangle$ . By the dilation operator  $e^{i\theta_j({}^i T_2)}$ , acting in the manner of Eq. (22), we may set the optimum scale

---

\* Henceforth the realization of generators will be given in the variables  $\vec{s}_i$  instead of  $\vec{r}_i$ . For instance  ${}^i T_2$  means  $-i(s_i \partial / \partial s_i + 1)$  instead of  $-i(r_i \partial / \partial r_i + 1)$ .

parameters which correspond to the effective nuclear charges of the electrons. Here we use the realization given in the previous section for the group operators and bases. Let us write

$$\mathcal{I}_A = D_{\theta_1, \theta_2, \theta'_1, \theta'_2} \left\{ b_1 \varphi_{PQLM}^{(n_1, n_2)} + b_2 \varphi_{PQLM}^{RS} \right\}, \quad (43-a)$$

and

$$\mathcal{I}_B = b_1 D_{\theta_1, \theta_2, \theta'_1, \theta'_2} \varphi_{PQLM}^{(n_1, n_2)} + b_2 \varphi_{PQLM}^{RS}, \quad (43-b)$$

where  $\varphi_{PQLM}^{(n_1, n_2)} \equiv |(n_1, n_2) PQLM\rangle$ ,  $\varphi_{PQLM}^{RS} \equiv |RS PQLM\rangle$  and

$D_{\theta_1, \theta_2, \theta'_1, \theta'_2} \equiv \frac{1}{2} \left\{ e^{i\theta_1(T_{1z})} e^{i\theta_2(T_{2z})} + e^{i\theta'_1(T'_{1z})} e^{i\theta'_2(T'_{2z})} \right\}$ . We begin by letting  $\theta_1 = \theta_2 = \theta'_1 = \theta'_2 = 0$ .

Later, for the ground state of helium, we will choose  $\theta_1 = \theta_2 = \theta'_1 = \theta'_2 \equiv \theta$  so as to minimize the energy of the state  $D_{0000} \varphi_{0000}^{(1,1)}$  \* with respect to  $\theta$ , and also we will choose  $\theta_1 = \theta'_1 \equiv \theta$  and  $\theta_2 = \theta'_2 \equiv \theta'$  so as to minimize the energy of the state  $D_{0000} \varphi_{0000}^{(1,1)}$  with respect to  $\theta$  and  $\theta'$ . †

Factors  $b_1$  and  $b_2$  will be determined by minimization of the energy expectation value, and the ratio  $b_2/b_1$  must vanish when  $Z$  goes to infinity. The function  $\varphi_{PQLM}^{(n_1, n_2)}$  is constructed from the one-electron functions  $\chi_{n_1 l_1 m_1}^{(\vec{s}_1)}$  of Eq. (18) :

$$\varphi_{PQLM}^{(n_1, n_2)} = \sum_{l_1, m_1, l_2, m_2} d_{n_1 l_1 m_1, n_2 l_2 m_2 : PQLM} \chi_{n_1 l_1 m_1}^{(\vec{s}_1)} \chi_{n_2 l_2 m_2}^{(\vec{s}_2)} \quad (44)$$

\* For the ground state of the helium atom, only the set of quantum numbers  $(n_1, n_2, P, Q, L, M) = (1, 1, 0, 0, 0, 0)$  is possible.

† See page 71-76.

where  $d_{n_1 l_1 m_1, n_2 l_2 m_2 : PQLM}$  are the  $SO(4)$  Wigner coefficients,<sup>(48)</sup> which satisfy the requirement

$$\sum_{l_1 m_1, l_2 m_2} |d_{n_1 l_1 m_1, n_2 l_2 m_2 : PQLM}|^2 = 1. \quad (45)$$

The function  $\varphi_{PQLM}^{RS}$  is constructed as

$$\begin{aligned} \varphi_{PQLM}^{RS} &= \sum_{n_1 n_2} C_{n_1 n_2}^{RS} \varphi_{PQLM}^{(n_1 n_2)} \\ &= \sum_{n_1 l_1 m_1, n_2 l_2 m_2} C_{n_1 n_2}^{RS} d_{n_1 l_1 m_1, n_2 l_2 m_2 : PQLM} \chi_{n_1 l_1 m_1}^{(\vec{S}_1)} \chi_{n_2 l_2 m_2}^{(\vec{S}_2)} \\ &\equiv \sum_{n_1 l_1 m_1, n_2 l_2 m_2} f_{n_1 l_1 m_1, n_2 l_2 m_2 : RSPQLM} \chi_{n_1 l_1 m_1}^{(\vec{S}_1)} \chi_{n_2 l_2 m_2}^{(\vec{S}_2)}. \end{aligned} \quad (46)$$

where  $f_{n_1 l_1 m_1, n_2 l_2 m_2 : RSPQLM}$  are the  $SO(4,1)$  Wigner coefficients and satisfy the condition

$$\sum_{n_1 l_1 m_1, n_2 l_2 m_2} |f_{n_1 l_1 m_1, n_2 l_2 m_2 : RSPQLM}|^2 = 1. \quad (47)$$

3-3 The Configuration Mixing due to several possible  
Two-Particle SO(4,1) Symmetries and the Ground State  
Wave Function of the Helium Atom

For the ground state of the helium atom, only the set of quantum numbers (PQLM) = (0000) is possible because of the condition,  $n_1=n_2=1$ . Furthermore the labeling  $Q=0$  must require  $S=0$ , because the fourth-order Casimir operator of SO(4,1) vanishes if  $Q=0$  for its SO(4) subgroup. (41,37) Therefore Eqs.(43-a,b) become

$$\Phi = b_1 \varphi_{0000}^{(1,1)} + b_2 \varphi_{0000}^{R'0}, \quad (48)$$

letting  $\theta_1 = \theta_2 = \theta'_1 = \theta'_2 = 0$ . According to Eqs.(44) and (46) the functions  $\varphi_{0000}^{(1,1)}$  and  $\varphi_{0000}^{R'0}$  are written as

$$\varphi_{0000}^{(1,1)} = d_{100,100:0000} \chi_{100}^{(\vec{s}_1)} \chi_{100}^{(\vec{s}_2)} = \chi_{100}^{(\vec{s}_1)} \chi_{100}^{(\vec{s}_2)}, \quad (49)$$

and

$$\varphi_{0000}^{R'0} = \sum_{n_1, n_2, l, m} f_{n_1, l, m, n_2, l-m: R'00000} \chi_{n_1, l, m}^{(\vec{s}_1)} \chi_{n_2, l-m}^{(\vec{s}_2)}. \quad (50)$$

Here we chose the phase factor of the SO(4) Wigner coefficients so that  $d_{100,100:0000} = 1$ . For a simple approximation to  $\varphi_{0000}^{R'0}$  we try the following function to see if it is physically realistic.

$$\varphi_{0000}^{R'0} \approx C_{11}^{R'0} \varphi_{0000}^{(1,1)} + C_{22}^{R'0} \varphi_{0000}^{(2,2)} + (C_{12}^{R'0} \varphi_{0000}^{(1,2)} + C_{21}^{R'0} \varphi_{0000}^{(2,1)}) \quad (51)$$

Here

$$C_{11}^{R'0} \varphi_{0000}^{(1,1)} = C_{11}^{R'0} \cdot \chi_{100}^{(\vec{s}_1)} \chi_{100}^{(\vec{s}_2)} \equiv C_{11}^{R'0} \cdot \Psi_1, \quad (52)$$

$$\begin{aligned} C_{22}^{R'0} \varphi_{0000}^{(2,2)} &= C_{22}^{R'0} \left[ -\frac{1}{2} \chi_{200}^{(\vec{s}_1)} \chi_{200}^{(\vec{s}_2)} + \frac{\sqrt{3}}{2} \cdot \frac{1}{\sqrt{3}} \left\{ \chi_{211}^{(\vec{s}_1)} \chi_{211}^{(\vec{s}_2)} - \chi_{210}^{(\vec{s}_1)} \chi_{210}^{(\vec{s}_2)} + \chi_{21-1}^{(\vec{s}_1)} \chi_{21-1}^{(\vec{s}_2)} \right\} \right] \\ &= C_{22}^{R'0} \cdot \frac{1}{2} \left\{ -\chi_{200}^{(\vec{s}_1)} \chi_{200}^{(\vec{s}_2)} + \chi_{211}^{(\vec{s}_1)} \chi_{211}^{(\vec{s}_2)} - \chi_{210}^{(\vec{s}_1)} \chi_{210}^{(\vec{s}_2)} + \chi_{21-1}^{(\vec{s}_1)} \chi_{21-1}^{(\vec{s}_2)} \right\} \\ &\equiv C_{22}^{R'0} \cdot \Psi_2, \end{aligned} \quad (53)$$

$$\begin{aligned} C_{12}^{R'0} \varphi_{0000}^{(1,2)} + C_{21}^{R'0} \varphi_{0000}^{(2,1)} &= (C_{12}^{R'0} d_{100,200:0000} \sqrt{2}) \cdot \frac{1}{\sqrt{2}} \left\{ \chi_{100}^{(\vec{s}_1)} \chi_{200}^{(\vec{s}_2)} + \chi_{200}^{(\vec{s}_1)} \chi_{100}^{(\vec{s}_2)} \right\} \\ &\equiv (C_{12}^{R'0} d_{100,200:0000} \sqrt{2}) \cdot \Psi_3. \end{aligned} \quad (54)$$

We can write Eq. (51) as

$$\begin{aligned} \varphi_{0000}^{R'0} &\approx C_{11}^{R'0} \cdot \Psi_1 + C_{22}^{R'0} \cdot \Psi_2 + (C_{12}^{R'0} d_{100,200:0000} \sqrt{2}) \cdot \Psi_3 \\ &\equiv C_1 \Psi_1 + C_2 \Psi_2 + C_3 \Psi_3. \end{aligned} \quad (55)$$

To obtain the coefficients  $C_1$ ,  $C_2$  and  $C_3$ , we will make use of the following eigenequations :

$${}^{12}C_{SO(4,1)}^{(2)} |RSPQLM\rangle = C^{(2)}(R,S) |RSPQLM\rangle, \quad (56)$$

$${}^{12}C_{SO(4,1)}^{(4)} |RSPQLM\rangle = C^{(4)}(R,S) |RSPQLM\rangle, \quad (57)$$

$$\{({}^{12}A)^2 + ({}^{12}L)^2\} |RSPQLM\rangle = \{P(P+2) + Q^2\} |RSPQLM\rangle, \quad (58)$$

$$\{({}^{12}A) \cdot ({}^{12}L)\}^2 |RSPQLM\rangle = \{Q(P+1)\}^2 |RSPQLM\rangle, \quad (59)$$

$$({}^{12}L)^2 |RSPQLM\rangle = L(L+1) |RSPQLM\rangle, \quad (60)$$

$$({}^{12}L)_z |RSPQLM\rangle = M |RSPQLM\rangle, \quad (61)$$

where  ${}^{12}C_{SO(4,1)}^{(2)}$  and  ${}^{12}C_{SO(4,1)}^{(4)}$  are the second-order and fourth-order Casimir operators of the two-particle  $SO(4,1)$  group mentioned in the previous section, and  $C^{(2)}(R,S)$  and  $C^{(4)}(R,S)$  are the eigenvalues of these operators. The generators  ${}^{12}L$ ,  ${}^{12}A$ ,  ${}^{12}B$ ,  ${}^{12}T$ ,  ${}^{12}T_2$ ,  ${}^{12}T_1$  are given by one of the sets of operators, ( i ), ( ii ), ( iii ), ( iv ) in page 60 . We will determine the coefficients  $C_1$ ,  $C_2$  and  $C_3$ , which satisfy all the equations (56)~(61) for our approximate eignestate  $\sum_{i=1}^3 C_i \Psi_i$  . From Eqs. (52)~(54), it is obvious that we have (60) and (61) true for any choice of the numbers  $C_1$ ,  $C_2$ ,  $C_3$  . If we have numbers

$C_1, C_2, C_3$ , which satisfy Eq. (58), that is

$$\left\{ ({}^{12}A)^2 + ({}^{12}L)^2 \right\} \left( \sum_{i=1}^3 C_i \psi_i \right) = 0, \quad (62)$$

we will automatically have Eq. (59) approximately true, because the condition  $P(P+2)+Q^2=0$  requires  $P=Q=0$ . This fact also requires that in Eq. (57) we have  $C^{(4)}(R',0)=0$ . Now we know that the  $C_1, C_2$  and  $C_3$  can be approximately determined by solving the eigenvalue problems of (56) and (58) simultaneously using the basis states  $\psi_1, \psi_2$  and  $\psi_3$ , that is

$${}^{12}C_{SO(4,1)}^{(2)} \chi^i = C^{(2)}(R^i,0) \cdot \chi^i, \quad (63)$$

$$\left\{ ({}^{12}A)^2 + ({}^{12}L)^2 \right\} \chi^i = 0 \cdot \chi^i, \quad (64)$$

where  $\chi^i = \gamma_1^i \psi_1 + \gamma_2^i \psi_2 + \gamma_3^i \psi_3$ . One of the vectors  $\chi^i = {}^t(\gamma_1^i, \gamma_2^i, \gamma_3^i)$ ;  $i=1,2,3$ , may correspond to the vector  $\chi_0 \equiv {}^t(C_1, C_2, C_3)$ . The operator  ${}^{12}C_{SO(4,1)}^{(2)}$  can be given in four different ways according to four different algebras (i), (ii), (iii), (iv) of page 60 :

$$C_i = ({}^1T_2 + {}^2T_2)^2 + ({}^1B - {}^2B)^2 - ({}^1L + {}^2L)^2 - ({}^1A - {}^2A)^2, \quad (65)$$

$$C_{ii} = ({}^1T_2 - {}^2T_2)^2 + ({}^1B + {}^2B)^2 - ({}^1L + {}^2L)^2 - ({}^1A - {}^2A)^2, \quad (66)$$

$$C_{iii} = ({}^1T_1 + {}^2T_1)^2 + ({}^1T - {}^2T)^2 - ({}^1L + {}^2L)^2 - ({}^1A - {}^2A)^2, \quad (67)$$

$$C_{iv} = ({}^1T_1 - {}^2T_1)^2 + ({}^1T + {}^2T)^2 - ({}^1L + {}^2L)^2 - ({}^1A - {}^2A)^2. \quad (68)$$



Now we solve the eigenvalue problem of (63) using the bases  $\Psi_1, \Psi_2$  and  $\Psi_3$ . We write Eq.(63) in the matrix form :

$$\underline{C}_\alpha \underline{x}_\alpha^i = \xi_\alpha^i \underline{x}_\alpha^i, \quad (69)$$

where the subscript  $\alpha$  means i, ii, iii or iv and the  $\xi_\alpha^i$  means  $C^{(2)}(R^i, 0)$  for the algebra ( $\alpha$ ). The matrix  $\underline{C}_\alpha$  is written as

$$\underline{C}_\alpha = [\langle \Psi_i | C_\alpha | \Psi_j \rangle] \equiv \left[ \int \int \Psi_i^* C_\alpha \Psi_j \cdot s_1 ds_1 d\omega_1 \cdot s_2 ds_2 d\omega_2 \right], \quad (70)$$

( $i, j = 1, 2, 3$ )

with the eigenvectors  $\underline{x}_\alpha^i = {}^t(y_{1\alpha}^i, y_{2\alpha}^i, y_{3\alpha}^i)$ . In order to obtain the matrix elements  $\langle \Psi_i | C_\alpha | \Psi_j \rangle$ , we need to calculate the integrals  $\langle \chi_{n_1 l_1 m_1}^{(S_1)} \chi_{n_2 l_2 m_2}^{(S_2)} | C_\alpha | \chi_{n_1 l_1 m_1}^{(S_1)} \chi_{n_2 l_2 m_2}^{(S_2)} \rangle$ . These integrations are easily carried out using the formulation in Appendix III and the matrix representations of the SO(4,1) generators in section 3-1. The results obtained for the cases (i), (ii), (iii), (iv) are :

	(i)			(ii)			(iii)			(iv)		
$\underline{C}_\alpha$	$\begin{pmatrix} 4 & 2 & 0 \\ 2 & 10 & 0 \\ 0 & 0 & 5 \end{pmatrix}$			$\begin{pmatrix} 4 & -2 & 0 \\ -2 & 10 & 0 \\ 0 & 0 & 3 \end{pmatrix}$			$\begin{pmatrix} 4 & -2 & 0 \\ -2 & 10 & 0 \\ 0 & 0 & 5 \end{pmatrix}$			$\begin{pmatrix} 4 & 2 & 0 \\ 2 & 10 & 0 \\ 0 & 0 & 3 \end{pmatrix}$		
$\xi_\alpha^i$	$7+\sqrt{13}$	$7-\sqrt{13}$	5	$7+\sqrt{13}$	$7-\sqrt{13}$	3	$7+\sqrt{13}$	$7-\sqrt{13}$	5	$7+\sqrt{13}$	$7-\sqrt{13}$	3
$\underline{x}_\alpha^i$	$\begin{pmatrix} 0.290 \\ 0.957 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.957 \\ -0.290 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$	$\begin{pmatrix} 0.290 \\ -0.957 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.957 \\ 0.290 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$	$\begin{pmatrix} 0.290 \\ -0.957 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.957 \\ 0.290 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$	$\begin{pmatrix} 0.290 \\ 0.957 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.957 \\ -0.290 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

(71)

We have shown that our eigenstate  $\sum_{i=1}^3 c_i \psi_i$  must approximately satisfy Eq. (64). The matrix representation of the 1st Casimir operator of  $SO(4)$  is

$$\underline{C}_{SO(4)} \equiv \left[ \langle \psi_i | ({}^{12}A)^2 + ({}^{12}L)^2 | \psi_j \rangle \right] = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 3 \end{pmatrix}, \quad (72)$$

with the eigenvectors  $\chi_\alpha^i = ({}^t \chi_{1\alpha}^i, \chi_{2\alpha}^i, \chi_{3\alpha}^i)$ . The vector  $\chi_0 = ({}^t c_1, c_2, c_3)$  must approximately satisfy the equation  $\underline{C}_{SO(4)} \chi_0 = 0 \cdot \chi_0$ . From (71) and (72) it is clear that the vectors of  $(0, 0, 1)$  do not satisfy this relation, and they must be eliminated from consideration. Therefore our equation of (48) will become one of the following equations :

$$\Phi^1 = \left\{ (\beta^1 + 0.290) \psi_1 + (0.957) \psi_2 \right\} \frac{1}{\sqrt{(\beta^1 + 0.290)^2 + (0.957)^2}}, \quad (73 \text{ -a})$$

$$\Phi^2 = \left\{ (\beta^2 + 0.957) \psi_1 - (0.290) \psi_2 \right\} \frac{1}{\sqrt{(\beta^2 + 0.957)^2 + (0.290)^2}}, \quad (73 \text{ -b})$$

$$\Phi^3 = \left\{ (\beta^3 + 0.290) \psi_1 - (0.957) \psi_2 \right\} \frac{1}{\sqrt{(\beta^3 + 0.290)^2 + (0.957)^2}}, \quad (73 \text{ -c})$$

$$\Phi^4 = \left\{ (\beta^4 + 0.957) \psi_1 + (0.290) \psi_2 \right\} \frac{1}{\sqrt{(\beta^4 + 0.957)^2 + (0.290)^2}}, \quad (73 \text{ -d})$$

where  $\beta^i$  are the variation parameters which correspond to  $(b_1 / b_2)$ . These expressions clearly show that the configuration mixing due to our two-particle  $SO(4,1)$  symmetry cannot

allow us the mixing in of a (1s)(2s) configuration which is written as  $\Psi_3 = \frac{1}{\sqrt{2}} \{ \chi_{100}^{(\vec{s}_1)} \chi_{200}^{(\vec{s}_2)} + \chi_{200}^{(\vec{s}_1)} \chi_{100}^{(\vec{s}_2)} \}^*$ .

If our approach is reasonable, the result obtained by diagonalizing the Hamiltonian matrix using the bases  $(1s)^2$ ,  $(1s)(2s)$ ,  $(2s)^2$ , and  $(2p)^2$  must show a quite small contribution of the  $(1s)(2s)$  configuration. Also the ratio of  $(2s)^2$  to  $(2p)^2$  in the result must be approximately that of  $\varphi_{0000}^{(2,2)}$ . These bases are defined as

$$(1s)^2 \sim \varphi_1 = \chi_{100}^{(\vec{s}_1)} \chi_{100}^{(\vec{s}_2)}, \quad (74-a)$$

$$(1s)(2s) \sim \varphi_2 = \frac{1}{\sqrt{2}} \{ \chi_{100}^{(\vec{s}_1)} \chi_{200}^{(\vec{s}_2)} + \chi_{200}^{(\vec{s}_1)} \chi_{100}^{(\vec{s}_2)} \}, \quad (74-b)$$

$$(2s)^2 \sim \varphi_3 = \chi_{200}^{(\vec{s}_1)} \chi_{200}^{(\vec{s}_2)}, \quad (74-c)$$

$$(2p)^2 \sim \varphi_4 = \frac{1}{\sqrt{3}} \{ \chi_{211}^{(\vec{s}_1)} \chi_{21-1}^{(\vec{s}_2)} - \chi_{210}^{(\vec{s}_1)} \chi_{210}^{(\vec{s}_2)} + \chi_{21-1}^{(\vec{s}_1)} \chi_{211}^{(\vec{s}_2)} \}. \quad (74-d)$$

Setting the trial wave function  $\Psi = \sum_{i=1}^4 \alpha_i \varphi_i$ , we can determine the coefficients  $\alpha_i$  by minimization of the energy expectation value  $E = \frac{\iint \Psi^* H \Psi d\tau_1 d\tau_2}{\iint \Psi^* \Psi d\tau_1 d\tau_2}$ .

Here the  $d\tau_i$  mean the volume elements  $s_i^2 ds_i d\omega_i$ . For the ground state, the result is

$$\Psi = (0.9790) \varphi_1 - (0.1978) \varphi_2 - (0.0257) \varphi_3 + (0.0419) \varphi_4. \quad (75)$$

$$\left[ \langle \Psi | \Psi \rangle = \iint \Psi^* \Psi \cdot s_1 ds_1 d\omega_1 \cdot s_2 ds_2 d\omega_2 \doteq 1 \right]$$

\* See Appendix IV.

As we see here, the contribution of (1s)(2s) is quite important for the ground state. Hence we conclude that the wave function  $\Psi_A$  or  $\Psi_B$  of Eq. (43), with  $\theta_1 = \theta_2 = \theta'_1 = \theta'_2 \equiv 0$ , is not a good approximation to the actual wave function. However the term,  $-(0.0257)\psi_3 + (0.0417)\psi_4$ , in Eq. (75) is approximately the state  $\varphi_{0000}^{(2,2)}$ , and again it suggests that the two-particle SO(4) generators  ${}^2\mathcal{L} = {}^1\mathcal{L} + {}^2\mathcal{L}$ ,  ${}^2\mathcal{A} = {}^1\mathcal{A} - {}^2\mathcal{A}$  are physically important operators.

We consider next the wave functions  $\Psi_A$ ,  $\Psi_B$  with  $\theta_1 = \theta_2 = \theta'_1 = \theta'_2 \equiv \theta$  which minimizes the energy of the function  $D_{\theta\theta\theta\theta} \varphi_{0000}^{(1,1)}$  with respect to  $\theta$ . Starting from the functions  $\Phi^i$  of Eqs. (73-a)-(73-d), we try to obtain the proper functions  $\Psi_A$  and  $\Psi_B$  changing the scale of the basis functions in the manner of Eqs. (43-a,b). Let us write

$$\Psi_{A-1}^i = N_{A-1}^i \cdot D_S \left\{ \beta^i \varphi_{0000}^{(1,1)} + \varphi_{0000}^{R^i 0} \right\}, \quad (76-a)$$

$$\Psi_{B-1}^i = N_{B-1}^i \cdot \left\{ \beta^i \cdot D_S \varphi_{0000}^{(1,1)} + \varphi_{0000}^{R^i 0} \right\}. \quad (76-b)$$

Here

$$D_S \equiv D_{\theta\theta\theta\theta} = e^{i\theta({}^1T_2)} e^{i\theta({}^2T_2)}; \quad \theta = \ln\left(\frac{S}{Z}\right) = \ln\left(\frac{S}{2}\right), \quad (77)$$

and  $N_{A-1}^i$ ,  $N_{B-1}^i$  are normalization constants:

$$\langle \Psi_{(B)-1}^i | \Psi_{(B)-1}^i \rangle = \iint \Psi_{(A)-1}^{i*} \Psi_{(A)-1}^i \cdot s_1 ds_1 d\omega_1 \cdot s_2 ds_2 d\omega_2 = 1. \quad (78)$$

The functions  $\{\beta^i \varphi_{0000}^{(1,1)} + \varphi_{0000}^{R^i}\}$  represent the starting functions  $\Phi^i$  of equations (73), without normalization coefficients :

$$\Phi^i \propto \beta^i \varphi_{0000}^{(1,1)} + \varphi_{0000}^{R^i} . \quad (79)$$

We use the well known value <sup>(49)</sup>

$$J = \frac{27}{16} = 1.6875 , \quad (80)$$

which makes  $\frac{\partial}{\partial J} \{D_J \varphi_{0000}^{(1,1)}\} = 0$  . The values of  $\beta^i$  will be determined by extremizing the overlap between  $\Psi$  and  $\Psi_{A-1}^i$  ,  $\Psi$  and  $\Psi_{B-1}^i$  , where  $\Psi$  is the wave function obtained by diagonalizing the Hamiltonian matrix [ Eq.(75) ] .

Therefore we require

$$\frac{\partial}{\partial \beta^i} \langle \Psi | \Psi_{A-1}^i \rangle = \frac{\partial}{\partial \beta^i} \iint \Psi^* \Psi_{A-1}^i \cdot s_1 ds_1 d\omega_1 \cdot s_2 ds_2 d\omega_2 = 0 , \quad (81-a)$$

$$\frac{\partial}{\partial \beta^i} \langle \Psi | \Psi_{B-1}^i \rangle = \frac{\partial}{\partial \beta^i} \iint \Psi^* \Psi_{B-1}^i \cdot s_1 ds_1 d\omega_1 \cdot s_2 ds_2 d\omega_2 = 0 . \quad (81-b)$$

We obtain the following results :

$$\Psi_{A-1}^{\frac{1}{2} \frac{3}{4}} = \begin{matrix} + & - & - & + \\ - & + & + & - \\ + & - & - & + \end{matrix} (0.9837)\varphi_1 + (0.1713)\varphi_2 + (0.0237)\varphi_3 - (0.0410)\varphi_4 , \quad (82)$$

$$\langle \Psi | \Psi_{A-1}^{\frac{1}{2} \frac{3}{4}} \rangle = \begin{matrix} + \\ - \\ + \end{matrix} (0.9992) , \quad (83)$$

$$\left(\beta_4^{\frac{1}{2}}\right)^{-1} = \begin{pmatrix} 0.0601 \\ -0.1643 \\ -0.0581 \\ 0.2396 \end{pmatrix}, \quad (84)$$

and

$$\Psi_{B-1}^1 = (0.9853)\varphi_1 - (0.1641)\varphi_2 - (0.0236)\varphi_3 + (0.0409)\varphi_4, \quad (85-1)$$

$$\Psi_{B-1}^2 = -(0.9790)\varphi_1 + (0.1983)\varphi_2 + (0.0246)\varphi_3 - (0.0425)\varphi_4, \quad (85-2)$$

$$\Psi_{B-1}^3 = -(0.9842)\varphi_1 + (0.1697)\varphi_2 + (0.0252)\varphi_3 - (0.0437)\varphi_4, \quad (85-3)$$

$$\Psi_{B-1}^4 = (0.9883)\varphi_1 - (0.1509)\varphi_2 - (0.0116)\varphi_3 + (0.0200)\varphi_4, \quad (85-4)$$

$$\langle \Psi | \Psi_{B-1}^{\frac{1}{2}} \rangle = \begin{pmatrix} 0.9994 \\ -1.0000 \\ -0.9996 \\ 0.9985 \end{pmatrix}, \quad (86)$$

$$\left(\beta_4^{\frac{1}{2}}\right)^{-1} = \begin{pmatrix} 0.0577 \\ -0.1673 \\ -0.0593 \\ 0.1128 \end{pmatrix}. \quad (87)$$

Finally we consider wave functions  $\Psi_A$ ,  $\Psi_B$  with  $\theta_1 = \theta'_2 \equiv \theta$  and  $\theta_2 = \theta'_1 \equiv \theta'$  ( $\theta \neq \theta'$ ) so as to minimize

the energy of the state  $D_{\theta\theta'\theta\theta} \varphi_{0000}^{(1,1)}$  with respect to both  $\theta$  and  $\theta'$ . Let us write

$$\Psi_{A-2}^i = N_{A-2}^i \cdot D_{SS'} \left\{ \beta^i \varphi_{0000}^{(1,1)} + \varphi_{0000}^{R^i} \right\}, \quad (88-a)$$

$$\Psi_{B-2}^i = N_{B-2}^i \cdot \left\{ \beta^i \cdot D_{SS'} \varphi_{0000}^{(1,1)} + \varphi_{0000}^{R^i} \right\}. \quad (88-b)$$

Here

$$D_{SS'} \equiv D_{\theta\theta'\theta\theta} = \frac{1}{2} \left\{ e^{i\theta(T_2)} e^{i\theta'(2T_2)} + e^{i\theta'(T_2)} e^{i\theta(2T_2)} \right\}; \quad (89)$$

$$\theta = \ln\left(\frac{J}{2}\right), \quad \theta' = \ln\left(\frac{J'}{2}\right),$$

and  $N_{A-2}^i$ ,  $N_{B-2}^i$  are normalization constants :

$$\langle \Psi_{(A)}^i | \Psi_{(B)}^i \rangle = 1. \quad (90)$$

The condition  $\frac{\partial}{\partial J} \left\{ D_{SS'} \varphi_{0000}^{(1,1)} \right\} = \frac{\partial}{\partial J'} \left\{ D_{SS'} \varphi_{0000}^{(1,1)} \right\} = 0$  is satisfied

$$\text{for } J = 1.1885, \quad J' = 2.1732. \quad (50) \quad (91)$$

Requiring

$$\frac{\partial}{\partial \beta^i} \langle \Psi | \Psi_{(A)}^i \rangle = 0, \quad (92)$$

we obtain the following results.

$$\Psi_{A-2}^{\frac{1}{2}\frac{3}{4}} = \begin{matrix} + & - & - & + \\ - & + & + & - \\ + & - & - & + \end{matrix} \begin{matrix} (0.9761)\psi_1 \\ (0.2124)\psi_2 \\ (0.0236)\psi_3 \\ (0.0408)\psi_4 \end{matrix}, \quad (93)$$

$$\langle \Psi | \Psi_{A-2}^{\frac{1}{2}\frac{3}{4}} \rangle = \begin{matrix} + \\ - \\ + \end{matrix} (0.9999) \quad (94)$$

$$\left(\beta_{\frac{3}{4}}^{\frac{1}{2}}\right)^{-1} = \begin{pmatrix} 0.0444 \\ -0.1271 \\ -0.0433 \\ 0.1679 \end{pmatrix}, \quad (95)$$

and

$$\Psi_{B-2}^1 = (0.9774)\psi_1 - (0.2057)\psi_2 - (0.0248)\psi_3 + (0.0429)\psi_4, \quad (96-1)$$

$$\Psi_{B-2}^2 = -(0.9774)\psi_1 + (0.2224)\psi_2 + (0.0161)\psi_3 - (0.0278)\psi_4, \quad (96-2)$$

$$\Psi_{B-2}^3 = -(0.9764)\psi_1 + (0.2105)\psi_2 + (0.0241)\psi_3 - (0.0417)\psi_4, \quad (96-3)$$

$$\Psi_{B-2}^4 = (0.9816)\psi_1 - (0.1867)\psi_2 - (0.0206)\psi_3 + (0.0356)\psi_4, \quad (96-4)$$

$$\langle \Psi | \Psi_{B-2}^{\frac{1}{2}\frac{3}{4}} \rangle = \begin{pmatrix} 1.0000 \\ -0.9995 \\ -0.9999 \\ 0.9999 \end{pmatrix}, \quad (97)$$

$$\left(\beta_{\frac{3}{4}}^{\frac{1}{2}}\right)^{-1} = \begin{pmatrix} 0.0398 \\ -0.0651 \\ -0.0373 \\ 0.1170 \end{pmatrix}. \quad (98)$$

We have found that the wave functions obtained by using approximate Hartree-Fock ground state functions



$D_{\theta_1, \theta_2, \theta_1', \theta_2'} \varphi_{0000}^{(1,1)}$  , together with a dilated or undilated configuration  $\varphi_{0000}^{R'0}$  , can be very good approximations to the ground state wave function obtained by a variational treatment with a Bednár  $(1s)^2, (1s)(2s), (2s)^2, (2p)^2$  basis. We have been able to obtain quite excellent overlaps with this ground state function, using  $\varphi_{0000}^{R'0}$  obtained from each of the four  $SO(4,1)$  groups we considered.

Further, and extensive, calculations will be required if one is to determine which of these groups is most valuable.

Appendix I

(51)

Z	Electrons pulled out	(I.P.) (eV)	$\left(\frac{I.P.}{n_{oe}}\right)^{ex} = \sqrt{\frac{2(I.P.)}{(27-2I)}}$	Z		(I.P.)	$\left(\frac{I.P.}{n_{oe}}\right)^{ex}$	Z		(I.P.)	$\left(\frac{I.P.}{n_{oe}}\right)^{ex}$			
1	H	1s	13.595	1.000	31	Ga	4p	6.00	0.644	61	Pm	6s	(5.55)	(0.639)
2	He	1s	24.580	1.344	32	Ge	4p	7.88	0.761	62	Sm	6s	(5.63)	(0.643)
3	Li	2s	5.390	0.629	33	As	4p	9.81	0.849	63	Eu	6s	(5.68)	(0.646)
4	Be	2s	9.320	0.828	34	Se	4p	9.75	0.847	64	Gd		(6.16)	
5	B	2p	8.296	0.781	35	Br	4p	11.84	0.933	65	Tb	6s	(5.85)	(0.656)
6	C	2p	11.264	0.910	36	Kr	4p	13.996	1.014	66	Dy	6s	(5.93)	(0.660)
7	N	2p	14.54	1.034	37	Rb	5s	4.176	0.554	67	Ho	6s	(6.02)	(0.665)
8	O	2p	13.614	1.000	38	Sr	5s	5.692	0.647	68	Er	6s	(6.10)	(0.670)
9	F	2p	17.42	1.132	39	Y	4d	6.5	0.691	69	Tm	6s	(6.18)	(0.674)
10	Ne	2p	21.559	1.259	40	Zr	5s	6.95	0.715	70	Yb	6s	(6.25)	(0.678)
11	Na	3s	5.138	0.615	41	Nb	5s	6.77	0.705	71	Lu		-	-
12	Mg	3s	7.644	0.750	42	Mo	5s	7.10	0.722	72	Hf		-	-
13	Al	3p	5.984	0.663	43	Te	5s	7.28	0.731	73	Ta	6s	7.88	0.761
14	Si	3p	8.149	0.774	44	Ru	5s	7.364	0.736	74	W	6s	7.98	0.766
15	P	3p	11.0	0.899	45	Rh	5s	7.46	0.740	75	Re	6s	7.87	0.761
16	S	3p	10.357	0.872	46	Pd	4d	8.33	0.782	76	Os	6s	8.7	0.800
17	Cl	3p	13.01	0.978	47	Ag	$4d^9 5s^2 \rightarrow 4d^{10}$	7.574	-	77	Ir	$1(4F_{7/2})$ $2(3F_4)$	9	-
18	Ar	3p	15.755	1.076	48	Cd	5s	8.991	0.813	78	Pt	6s	9.0	0.813
19	K	4s	4.339	0.565	49	In	5p	5.785	0.652	79	Au	6s	9.22	0.823
20	Ca	4s	6.111	0.670	50	Sn	5p	7.342	0.735	80	Hg	6s	10.43	0.876
21	Sc	4s	6.56	0.694	51	Sb	5p	8.639	0.797	81	Tl	6p	6.106	0.670
22	Ti	4s	6.83	0.709	52	Te	5p	9.01	0.814	82	Pb	6p	7.415	0.738
23	V	$3d^3 4s^2 \rightarrow 3d^4$	6.74	-	53	I	5p	10.454	0.877	83	Bi	6p	7.287	0.732
24	Cr	4s	6.763	0.705	54	Xe	5p	12.127	0.944	84	Po	$1(3P_2)$ $2(3S_{1/2})$	8.43	-
25	Mn	4s	7.432	0.739	55	Cs	6s	3.893	0.535	85	At		-	-
26	Fe	4s	7.90	0.762	56	Ba	6s	5.210	0.619	86	Rn	6p	10.746	0.889
27	Co	$3d^7 4s^2 \rightarrow 3d^8$	7.86	-	57	La	$5d^1 6s^2 \rightarrow 5d^2$	5.61	-	87	Fr		-	-
28	Ni	$3d^8 4s^2 \rightarrow 3d^9$	7.633	-	58	Ce	6s	(5.65)	(0.644)	88	Ra	7s	5.277	0.623
29	Cu	4s	7.724	0.753	59	Pr	6s	(5.42)	(0.631)	89	Ac		-	-
30	Zn	4s	9.391	0.831	60	Nd	6s	(5.49)	(0.635)	90	Th		-	-

## Appendix II

In the electron configuration scheme for atoms, the p, d, f electrons first appear at  $N=5, 21, 58$  (B, Sc, Ce). We may notice the atomic numbers of He, Ar, Xe (rare gas atoms of  $\nu=1, 3, 5$ )<sup>\*</sup> are very close to these numbers. Using this fact we will obtain a simple approximate expression  $N_0$  for the atomic numbers of rare gas atoms. The Thomas-Fermi approximation predicts<sup>(34)</sup> that the electrons of azimuthal quantum number  $l$  first appear in the atoms of nuclear charge  $0.155(2l+1)^3$ . If we use a coefficient 0.17 instead of 0.155, we have more accurate equation :

$$Z = 0.17(2l+1)^3 \tag{AII-1}$$

This gives correctly the numbers 5, 21, 58 for  $l=1, 2, 3$ , if we take the nearest integer  $Z$ .

The atomic numbers of rare gas atoms for  $\nu=1, 3, 5, 7, \dots$  are roughly given by Eq. (AII-1) for  $l=1, 2, 3, 4, \dots$ , and these  $\nu$  and  $l$  have a relation  $l = \frac{\nu+1}{2}$ . Then we may write

$$\left( \begin{array}{l} \text{Atomic number} \\ \text{of a rare gas atom} \end{array} \right) \approx N'_0 \equiv 0.17(\nu+2)^3 \tag{AII-2}$$

---

\* See page 26. The outer shells K, L, M, ... correspond to  $\nu=1, 2, 3, \dots$

The results of Eq. (AII-2) are listed on Tab. AII. Introducing a correction term into this equation, we have the following simple expression for  $N_0$ .

$$N_0 \equiv 0.17(\nu+2)^3 - \{1.9 + 0.7(-1)^{\nu+1}\}. \quad (\text{AII-3})$$

The results are also listed on Tab. AII.

Outer Shell	$\nu$	Atomic Numbers of Rare Gas Atoms	$N'_0$	$N_0$
K	1	2	4.6	2.0
L	2	10	10.9	9.7
M	3	18	21.2	18.6
N	4	36	36.7	35.5
O	5	54	58.3	55.7
P	6	86	87.0	85.8
Q	7	118		

Tab. AII

Appendix III

The integrals  $\langle \chi_{n_1 l_1 m_1}^{(\vec{s}_1)} \chi_{n_2 l_2 m_2}^{(\vec{s}_2)} | C_i | \chi_{n_1 l_1 m_1}^{(\vec{s}_1)} \chi_{n_2 l_2 m_2}^{(\vec{s}_2)} \rangle$   
are written in the following way for the case (i) :

$$\begin{aligned} & \langle \chi_{n_1 l_1 m_1}^{(\vec{s}_1)} \chi_{n_2 l_2 m_2}^{(\vec{s}_2)} | C_i | \chi_{n_1 l_1 m_1}^{(\vec{s}_1)} \chi_{n_2 l_2 m_2}^{(\vec{s}_2)} \rangle \\ &= \langle | ({}^1T_2 + {}^2T_2)^2 + ({}^1B - {}^2B)^2 - ({}^1L + {}^2L)^2 - ({}^1A - {}^2A)^2 | \rangle \\ &= \langle | \sum_{i=1}^2 \{ ({}^i T_2)^2 + ({}^i B)^2 - ({}^i L)^2 - ({}^i A)^2 \} + 2 \{ {}^1 T_2 {}^2 T_2 - {}^1 B {}^2 B - {}^1 L {}^2 L + {}^1 A {}^2 A \} | \rangle \\ &= 4 \cdot \delta_{n_1 m_1} \delta_{l_1 l_2} \delta_{m_1 m_2} \delta_{n_2 m_2} \delta_{l_2 l_2} \delta_{m_2 m_2} \\ & \quad - \frac{1}{2} \langle n_1 l_1 m_1 | {}^1 T_+ - {}^1 T_- | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | {}^2 T_+ - {}^2 T_- | n_2 l_2 m_2 \rangle \\ & \quad - \langle n_1 l_1 m_1 | {}^1 B_+ | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | {}^2 B_- | n_2 l_2 m_2 \rangle \\ & \quad - \langle n_1 l_1 m_1 | {}^1 B_- | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | {}^2 B_+ | n_2 l_2 m_2 \rangle \\ & \quad - 2 \cdot \langle n_1 l_1 m_1 | {}^1 B_3 | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | {}^2 B_3 | n_2 l_2 m_2 \rangle \\ & \quad - \langle n_1 l_1 m_1 | {}^1 L_+ | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | {}^2 L_- | n_2 l_2 m_2 \rangle \\ & \quad - \langle n_1 l_1 m_1 | {}^1 L_- | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | {}^2 L_+ | n_2 l_2 m_2 \rangle \\ & \quad - 2 \cdot \langle n_1 l_1 m_1 | {}^1 L_3 | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | {}^2 L_3 | n_2 l_2 m_2 \rangle \\ & \quad + \langle n_1 l_1 m_1 | {}^1 A_+ | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | {}^2 A_- | n_2 l_2 m_2 \rangle \\ & \quad + \langle n_1 l_1 m_1 | {}^1 A_- | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | {}^2 A_+ | n_2 l_2 m_2 \rangle \\ & \quad + 2 \cdot \langle n_1 l_1 m_1 | {}^1 A_3 | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | {}^2 A_3 | n_2 l_2 m_2 \rangle, \end{aligned}$$

where  $\langle n_1 l_1 m_1 | {}^i P | n_1 l_1 m_1 \rangle = \int \chi_{n_1 l_1 m_1}^{* (\vec{s}_1)} {}^i P \chi_{n_1 l_1 m_1}^{(\vec{s}_1)} \cdot s_i d s_i d \omega_i$ .

## Appendix IV

Examining the equation in Appendix III and the matrix representations of  $SO(4,1)$  generators in section 3-1, we understand the reason why the  $(1s)(2s)$  configuration does not mix with  $(2s)^2$ ,  $(2p)^2$  and  $(1s)^2$  configurations. For this kind of mixing, the matrix elements of the Casimir operator are given by  $\langle \chi_{100}^{(\vec{s}_1)} \chi_{100}^{(\vec{s}_2)} | C_\alpha | \chi_{100}^{(\vec{s}_1)} \chi_{200}^{(\vec{s}_2)} \rangle$  and  $\langle \chi_{100}^{(\vec{s}_1)} \chi_{200}^{(\vec{s}_2)} | C_\alpha | \chi_{2\ell m}^{(\vec{s}_1)} \chi_{2\ell-m}^{(\vec{s}_2)} \rangle$ . As we see in Appendix III, these elements consist of the terms

$$\langle 100 | {}^i P | 100 \rangle \langle 100 | {}^i P | 200 \rangle \quad \text{and} \quad \langle 100 | {}^i P | 2\ell m \rangle \langle 200 | {}^i P | 2\ell - m \rangle, \quad (A)$$

where  ${}^i P$  are the one-particle  $SO(4,1)$  generators. These  ${}^i P$  in (A) produce  $|n, \ell', m'\rangle$  or  $|n\pm 1, \ell'', m''\rangle$  operating on  $|n, \ell, m\rangle$ , but they can not produce the linear combination of  $|n, \ell', m'\rangle$  and  $|n\pm 1, \ell'', m''\rangle$ . Consequently all the terms of (A) vanish.

We also notice that the same kind of situation occurs for the two-particle  $SO(4,2)$  symmetry based on the realization given in section 3-1.

## REFERENCES

- ( 1 ) J. C. Slater, Quantum Theory of Atomic Structure, Vols. I-II, McGraw-Hill, New York, 1960.
- ( 2 ) D. I. Mendeleev, J. Russ. Phys. Chem. Soc. 1, 60 (1869).
- ( 3 ) W. Kossel, Ann. Physik, 49, 229 (1916).
- ( 4 ) G. N. Lewis, J. ACS, 38, 762 (1916).
- ( 5 ) I. Langmuir, J. ACS, 41, 868 (1919).
- ( 6 ) N. Bohr, Z. Physik, 9, 1 (1922).
- ( 7 ) G. E. Uhlenbeck and S. Goudsmit, Naturwiss., 13, 953 (1925);  
Nature, 117, 264 (1926).
- ( 8 ) W. Pauli, Jr., Z. Physik, 31, 765 (1926).
- ( 9 ) E. Madelung, Die Mathematischen Hilfsmittel des Physikers (Springer-Verlag, Berlin, 1936), Appendix 15 (Atombau) of 3rd. edition, p.359.
- (10) S. A. Goudsmit and P. I. Richards, Proc. Natl. Acad. Sci. USA, 51, 664 (1964).
- (11) E. Schrödinger, Z. Physik, 4, 347 (1921).  
D. R. Hartree, Proc. Cambridge Phil. Soc., 21, 625 (1923);  
22, 409 (1924).  
R. B. Lindsay, J. Math. and Phys., 3, 191 (1924).
- (12) H. G. J. Moseley, Phil. Mag. 26, 1024 (1913); 27, 703 (1914).
- (13) D. R. Hartree, Proc. Cambridge Phil. Soc., 24, 89, 111 (1928).
- (14) V. Fock, Z. Physik, 61, 126 (1930); 62, 795 (1930).
- (15) C. Zener, Phys. Rev., 36, 51 (1930).
- (16) J. C. Slater, Phys. Rev., 36, 57 (1930).
- (17) D. Layzer, Ann. Phys. (N. Y.) 8, 271 (1959).
- (18) See, for example, T. Kato, J. Fac. Sci. Tokyo, Sec. I 16,  
145 (1951).  
A. Dalgarno and G. W. F. Drake, Chem Phys. Lett. 3, 349 (1969).

- (19) R. M. Sternheimer, *Phys. Rev. A*, 15, 1817 (1977).
- (20) A. O. Barut, *The Structure of Matter*, in *Proc. Rutherford Centennial Symp.* ( University of Canterbury, 1971 ) p.126.
- (21) O. A. Navaro and K. B. Wolf, *Rev. Mex. Fis.*, 20, 265 (1971).
- (22) M. Berrondo and O. A. Navaro, *J. Phys. B: Atom. Molec. Phys.*, 6, 761 (1973).
- (23) V. M. Byakov et al., preprint, ITEP-90, Institute of Theoretical and Experimental Physics, Moscow (1976).
- (24) C. E. Wulfman, unpublished (1974).
- (25) R. L. Anderson, S. Kumei and C. E. Wulfman, *Rev. Mex. Fis.*, 21, 35 (1972).
- (26) A. O. Barut and H. Kleinert, *Phys. Rev.*, 156, 1541 (1967).
- (27) P. O. Löwdin, *Advances in Chemical Physics*, Vol. II, Interscience, New York, 1959, p. 207.
- H. Yoshizumi, *Advances in Chemical Physics*, Vol. II, Interscience, New York, 1959, p. 323.
- (28) C. Wulfman and S. Kumei, *Chem. Phys. Lett.*, 23, 367 (1973).
- (29) C. Wulfman, *Chem. Phys. Lett.*, 23, 370 (1973).
- (30) O. Sinanoğlu and D. R. Herrick, *J. Chem. Phys.*, 62, 886 (1975).
- D. R. Herrick and O. Sinanoğlu, *Phys. Rev. A*, 11, 97 (1975).
- (31) R. L. Anderson, S. Kumei and C. E. Wulfman, *Phys. Rev. Lett.*, 28, 988 (1972).
- (32) R. L. Anderson, S. Kumei and C. E. Wulfman, *Rev. Mex. Fis.*, 21, 1 (1972).
- (33) J. C. Slater, *Phys. Rev.* 98, 1039 (1955).
- (34) See, for example, L. D. Landau and E. M. Lifshiz, *Quantum Mechanics*, Addison- Wesley, Reading, Massachusetts (1965), Chap. 10.
- (35) E. P. Wigner, *Am. J. Math.*, 63, 57 (1941).



- (36) See, for example, B. G. Wybourne, Classical Groups for Physicists, Wiley-Interscience, Chap. 21, 1970.
- (37) A. Kihlberg and S. Ström, Ark. Fys., 31, 491 (1965).
- (38) T. Sumi, M. S. Thesis, University of the Pacific, 1977.
- (39) C. E. Wulfman and Y. Takahata, J. Chem. Phys., 47, 488 (1967).
- (40) I. M. Gel'fand and M. L. Zetlin, Dokl. Acad. Nauk., USSR, 71, 1017 (1950).
- I. M. Gel'fand, R. A. Minlos and Z. Ya. Shapilo, Representations of the Rotation - and Lorentz Groups and Their Application, The Macmillan Company, New York, 1963, p. 353.
- (41) A. Böhm, Nuovo Cimento, 43, 665 (1966).
- (42) S. C. Pang and K. T. Hecht, J. Math. Phys., 8, 1233 (1967).
- (43) Y. Nambu, Phys. Rev., 160, 1171 (1967).
- (44) A. O. Barut and G. L. Bornzin, J. Math. Phys., 12, 841 (1971).
- (45) M. Bednář, Ann. Phys., (N.Y.) 75, 305 (1973).
- (46) H. McIntosh, in Group Theory and Its Application, Vol. 2, ed. E. M. Loeb1 ( Academic Press, New York, 1971 ).
- (47) C. Wulfman, in Group Theory and Its Application, Vol. 2, ed. E. M. Loeb1 ( Academic Press, New York, 1971 ), p. 145.
- (48) L. C. Biedenharn, J. Math. Phys., 2, 433 (1961).
- (49) H. Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry, Van Nostrand, Princeton, New Jersey (1959),  
H. Eyring, J. Walter and G. E. Kimball, Quantum Chemistry, Wiley, New York (1960).
- (50) E. A. Hylleraas, Z. Physik, 54, 347 (1929),  
C. Eckart, Phys. Rev., 36, 878 (1930).
- (51) C. E. Moore, Atomic Energy Levels, Vols. I-III (1949-1958), Natl. Bur. Stand. Circ. No. 467 (Washington, D.C., U.S.GPO).