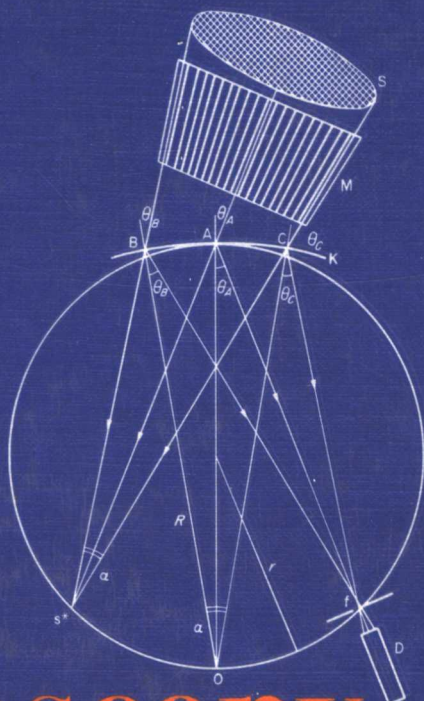


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# Advances in **X-Ray** Spectroscopy



(Contributions in Honour of  
Professor Y CAUCHOIS)

Editors:

**C BONNELLE**

*Université Pierre et Marie Curie, Paris, France*

**C MANDE**

*Nagpur University, India*

Pergamon Press

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**PERGAMON PRESS**

OXFORD · NEW YORK · TORONTO · SYDNEY · PARIS · FRANKFURT

<b>U.K.</b>	Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, England
<b>U.S.A.</b>	Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
<b>CANADA</b>	Pergamon Press Canada Ltd., Suite 104, 150 Consumers Road, Willowdale, Ontario M2J 1P9, Canada
<b>AUSTRALIA</b>	Pergamon Press (Aust.) Pty. Ltd., P.O. Box 544, Potts Point, N.S.W. 2011, Australia
<b>FRANCE</b>	Pergamon Press SARL, 24 rue des Ecoles, 75240 Paris, Cedex 05, France
<b>FEDERAL REPUBLIC OF GERMANY</b>	Pergamon Press GmbH, 6242 Kronberg-Taunus, Hammerweg 6, Federal Republic of Germany

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First edition 1982

#### **British Library Cataloguing in Publication Data**

Advances in X-ray spectroscopy.

I. Cauchois, Y. 2. X-ray spectroscopy—

Addresses, essays, lectures

I. Bonnelle, C. II. Mande, C.

III. Cauchois, Y.

537.5'352 QC482.S6

ISBN 0-08-025266-4

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#### *Cover Illustration*

This is taken from figure 3 on page 95 of the article  
"Bent Crystal Spectroscopy for X and  $\gamma$  - Radiations"  
by M. A. Blokhin

*Printed in Great Britain by A. Wheaton & Co. Ltd., Exeter*

## Foreword

PROFESSOR FRANCIS PERRIN

This book is dedicated to Professor Yvette Cauchois on her retirement as Director of the Laboratoire de Chimie Physique de l'Université Pierre et Marie Curie, Paris. It is a collection of papers written by specialists in the field of X-ray spectroscopy who wish to pay respect to the scientific work of Yvette Cauchois which she has carried out over a period of 50 years in this particular laboratory, which was founded, and for many years directed, by Jean Perrin. Her work has inspired many of the authors of the papers in this volume in their own research which has often been made possible thanks to the use of bent-crystal X-ray spectrographs, remarkable instruments which owe so much to Yvette Cauchois.

She first published the principle of this new type of instrument in 1931 with a description of its construction, as a note to the Comptes Rendus de l'Académie des Sciences, Paris, entitled "Spectrographe lumineux par transmission de rayons X non canalisés à travers un mica courbé". Thanks to the high luminosity and resolving power of spectrographs designed according to this principle, Yvette Cauchois was the first to measure the main emission lines of the K-series spectra of xenon and krypton where the gases were excited by means of an electron beam passing through a thin metallic window in a cathode tube. She then went on to discover very weak non-diagram emission lines for many elements, which were often satellites to the main lines of the L-series and which she interpreted as emissions from atoms multiply ionised in core levels through Auger effects. Measurement of the frequencies of these lines enabled the first precise determination of the corresponding energy levels, and leading from this work Yvette Cauchois was also the first to measure the characteristic X-ray spectra of radium and polonium which could only be studied in small or very small quantities.

This fine work on X-ray atomic spectra was carried out by Yvette Cauchois from 1930 to 1940. Following the considerable difficulties and scientific isolation brought about by the German wartime occupation of France, Yvette Cauchois directed the use of the powerful X-ray spectrographic methods which she had created towards the solution of problems in chemical physics. Thus, she studied modifications in outer unoccupied energy levels resulting from interactions between neighbouring atoms in a solid or a liquid. By concentrating on a study of the structure of the L-absorption edges, Yvette Cauchois obtained important data on the outer levels of bound atoms in a solid medium, in particular in metals. As an example of this work, the measurement of the nickel and copper absorption edges in alloys of various composition provided her with an explanation for the disappearance of ferromagnetism when copper is progressively added to nickel.

Since 1953, the date at which she was nominated "Professeur Titulaire" and Director of the Laboratoire de Chimie-Physique de la Faculté des Sciences de l'Université de Paris, Yvette Cauchois has continued her personal work and directed that of many research scientists. In particular, she has continued the development of bent-crystal spectrometers and applied them in the following fields:

(i) In atomic physics, where studies have been made of the characteristic X-ray spectra of transuranic elements, of the L- and M-series of plutonium and of the M-series of americium.

(ii) In solid-state physics, where she has used X-ray spectrometry to investigate defects created by high-energy radiation.

(iii) In nuclear physics, where determinations have been made of the natural width and hence the mean lifetime of the first excited states of many nuclei by measuring the self-absorption of nuclear fluorescence radiation excited by 1-2 MeV electron Br $\ddot{u}$ msstrahlung.

In addition, Yvette Cauchois was involved in the first spectral analysis of X-rays (in the 1.5-15 Å region) generated by synchrotron radiation and pioneered the use of the intense X-ray continuum provided in this spectral range by electron synchrotrons of a few GeV.

The scientific work of Yvette Cauchois thus occupies an important place in the development of X-ray physics over the past 50 years and her bent-crystal spectrographs have been used by specialists throughout the world for many years in the field of high-precision  $\gamma$ -ray spectrometry.

## Preface

Of the many types of spectroscopies available for the study of the structure of matter, X-ray spectroscopy, along with optical spectroscopy, was the first to contribute in a spectacular way to our knowledge of the electronic structure of atoms and condensed matter. In recent years X-ray spectroscopy has also revealed itself to be a very good method for the determination of interaction energies between nuclei and muons. In addition, effects due to the size of the nucleus are known to exist in X-ray spectra.

At the present time there is renewed interest in the method mainly due to the development of new X-ray-ultraviolet sources such as synchrotron radiation which are proving to be powerful tools for extending the investigations.

The analysis of X-ray transitions between atomic levels is a very direct manner of studying atomic structure: experimental determinations of the energy of X-ray lines and calculated values can be used side by side as a test of theoretical models. The first two papers in Part I illustrate this point. X-ray-ultraviolet photoabsorption measurements on atomic jets and vapours are of considerable interest for the same reason, and some of the correlation effects observed recently in such spectra are described in the third paper. The last two papers in this section are concerned with relativistic theories of X-ray emission satellites and electron Bremsstrahlung.

Part II is devoted to a review of the means provided by X-ray spectroscopy for the determination of the electronic structure of solids. The spectra from metals, semiconductors and insulators, whether in the form of the pure elements, alloys, or compounds, are discussed in relation to band structure calculations and many-body effects. The results concerning a large variety of compounds in the solid or gas phase are then discussed, usually with reference to a molecular orbital model. The section is concluded by a description of the many possibilities provided by X-ray emission and absorption measurements for the study of chemical bonding.

Over the past ten years methods have been developed with the aim of obtaining new types of information from X-ray spectra. Some of these are dealt with in Part III. The most recent of them concerns the determination of anisotropy of fluorescence emission as a means of studying molecular geometry. EXAFS spectroscopy, which has attracted much attention lately, and one of the aspects of Compton spectra are treated in some detail. Next, the possibilities opened up by resonant X-ray emissions and isochromat spectroscopies in the study of excitation states in solids are underlined. Lastly, an incisive description of the present state of research in the development of X-ray lasers is given.

This book would not be complete without an extensive description of the techniques available for such studies. They are presented in the last section (Part IV) and concern bent crystal and two-crystal spectrometers. There are also detailed studies of the reflecting properties of crystals in the X-ray region and a general review of X-ray optics. The development of these topics has been stimulated by the need for constant improvements in the analysis of X-radiation emitted by extraterrestrial sources and plasmas.

The reader, like the editors, may regret that some important aspects of X-ray physics have been left out. The reason has often been that other commitments and pressure of work have made it impossible for the specialists in the field to contribute. However, it is hoped that the list of several hundred references given in the book may help to fill the gap.

## Introduction

SIR NEVILL MOTT

*Cavendish Laboratory, Cambridge, UK*

It is a pleasure to contribute an introduction to this book, written on the occasion of her retirement, to mark the respect and admiration that the friends and colleagues of Professor Cauchois feel for her contribution to the science of X-ray spectra, to wider fields of scientific research and education, and to the scientific traditions of her country. Her first paper on "Un crystal courbé" was published in the *Comptes Rendus* in 1932; her doctorate, on the same subject, appeared in the *Annales de Physique* in the next year and there followed up to and during the war a series of papers on the soft X-ray emission and absorption of metals, of other solids and of gases. My first contact with this subject was in 1936, newly appointed to the University of Bristol, where the late Herbert Skinner was establishing the physical existence of a sharp Fermi cut-off in the emission bands of light metals; though aware of Mademoiselle Cauchois' work at that time, I did not have the opportunity of discussing it with her until those days, immediately after the war, when scientists from our two countries could once more visit each other and describe and compare with enthusiasm their results and ideas. I remember particularly discussions on the "raie blanche" in the absorption spectra of transition metals, having its origin in transitions from X-ray levels to unoccupied states in a d-band, and my pleasure in seeing this confirmation of my ideas on the band structure of these materials. Discussions on magnetic and electrical properties indeed gave evidence for these states, but when the X-ray spectra appeared it was like seeing them and "seeing is believing". I remember, too, lecturing in her Institute in the Rue Pierre-Curie (now Rue Pierre et Marie Curie), and introducing the idea of excitons, perhaps for the first time to that audience; later (in 1949) she and I wrote a short paper, trying to see what applications the idea of excitons could have to X-ray spectra. Throughout her career, and in addition to and supplemented by her



work on high-energy sources, she has continued to use X-ray spectroscopy as a tool for understanding the band structure and chemical bonding in solids.

Professor Cauchois, a pupil of Jean Perrin, retires from her post as Director of the Laboratoire de Chimie-Physique. Chimie-Physique is a concept generated by the genius of French science, not to be confused with the Physical Chemistry, Inorganic Chemistry or even the Chemical Physics of the English-speaking countries. Now we have both solid-state physics and solid-state chemistry, each with their appropriate journals. As a solid-state physicist, I have always felt completely at home on the scientific level in the laboratories of Chimie-Physique of France, and particularly the one in the Rue Pierre-Curie. It seems to me that in calling their subject chimie-physique, rather than physical chemistry or chemical physics, those responsible have affirmed their belief that the two subjects are equal and neither is subordinate to the other. It is hoped that this tradition will continue; it is certainly the way to make progress in the science of materials.

X-ray spectroscopy has become fashionable again recently. The theoretical work on the origin of the peak at the absorption edge in some metals, mainly carried out in France, and the development of EXAFS are two of the highlights. Throughout all these developments Professor Cauchois has remained a leader of the subject, in demand at all international conferences and indeed the organiser of some. All her friends will wish her continued scientific activity and success in her retirement.

# Contents

by author alphabetical sequence

Introduction	Sir Nevill Mott	xiii
Chapter 1	Relativistic Theory of X-Ray Satellites T. Aberg and M. Suvanen	1
Chapter 2	Electronic Structure of Metals and Alloys by X-Ray Spectroscopy L. V. Azaroff and D. M. Pease	36
Chapter 3	Understanding and Improving Crystals for X-Ray Fluorescence and Plasma Diagnostics L. S. Birks and D. B. Brown	58
Chapter 4	Nuclear Finite Size Effects in X-Ray Spectra F. Boehm	76
Chapter 5	Bent Crystal Spectroscopy for X- and $\gamma$ - Radiations M. A. Blokhin	90
Chapter 6	Resonant X-Ray Emission Spectroscopy in Solids C. Bonnelle	104
Chapter 7	From X-Ray to UV Physics with Synchrotron Radiation J. P. Connerade	122
Chapter 8	Comparison of Relativistic Atomic SCF Calculations with Improved Experimental Data R. D. Deslattes, L. Jacobs, E. G. Kessler, Jr and W. Schwitz	144
Chapter 9	Reflection of X-Rays by Bent Crystals J. Despujols, W. G. Burgers and T. J. Tiedema	153
Chapter 10	The Two-Crystal Spectrometer for X-Ray Spectroscopy J. Drahekoupil and A. Fingerland	167

Chapter 11	The So-Called Correction of Bragg's Law P. P. Ewald	202
Chapter 12	On the Anisotropic Emission of Characteristic X-Rays A. Faessler, E. Gilberg and G. Wiech	210
Chapter 13	Molecular Orbitals and X-Ray Spectra C. K. Jørgensen	225
Chapter 14	X-Ray Spectra of Molecular Gases R. E. LaVilla	240
Chapter 15	Many-Body Effects in X-Ray Band Spectra of Metals P. Longe	254
Chapter 16	The History and Modern Practice of EXAFS Spectroscopy F. W. Lytle, D. E. Sayers and E. A. Stern	267
Chapter 17	Chemical Shifts in X-Ray Absorption Spectra C. Mandé and V. B. Sapre	287
Chapter 18	Chemical Shifts and Changes in Shape of X-Ray Emission Lines in Solids A. Meisel	302
Chapter 19	X-Ray Optics M. Montel	338
Chapter 20	Potential Characteristics and Applications of X-Ray Lasers D. J. Nagel	371
Chapter 21	Electron Bremsstrahlung R. H. Pratt	411
Chapter 22	Band Structure of Semiconductors by X-Ray Spectroscopy C. Senemaud	423
Chapter 23	X-Ray Raman Band and Plasmon Line in the Compton Spectrum T. Suzuki	439
Chapter 24	Isochromat Spectroscopy K. Ulmer	451

## CHAPTER 1

# Relativistic Theory of X-ray Satellites

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### 1.1 INTRODUCTION

The influence of the relativistic motion of inner-shell electrons on the characteristic X-ray spectrum had already been recognised by Sommerfeld<sup>1</sup> in 1916. Along with the Pauli principle and the understanding of the equivalence of the one-hole and one-electron configurations, Dirac's relativistic quantum-theoretical model of hydrogen-like ions modified by screening constants became the basis for the interpretation of the so-called diagram X-ray lines (see, for example, Blokhin<sup>2</sup>). The non-diagram lines or X-ray satellites, which can usually be interpreted as one-electron transitions between multiply-ionised states or two-electron transitions<sup>3,4</sup>, have provided a much more difficult problem with regard to a proper treatment of relativistic effects. However, as we shall show, recent developments of the relativistic many-electron theory have opened new avenues in this respect.

Today the relativistic treatment, including quantum-electrodynamic (QED) corrections, is becoming increasingly important in the analysis of a diversity of complex X-ray spectra which are related to what is traditionally known as X-ray satellites. For instance, accurate relativistic calculations of transition energies and probabilities

may be needed for the identification of X-ray lines from multiply-ionised atoms in plasmas from terrestrial and celestial sources<sup>5</sup>.

The interpretation of X-ray spectra from heavy ion-atom collisions<sup>6</sup> and of X-ray line-shifts of chemical or nuclear origin<sup>7-9</sup> often requires an accurate relativistic analysis of the composition of the observed lines.

In all the examples mentioned above, as well as in the case of ordinarily excited X-ray satellite spectra, open-shell configurations are involved. Hence, special attention must be paid to such relativistic methods which are capable of handling defect configurations and their mixing as in the multiconfiguration Dirac-Fock (MCDF) method<sup>10</sup>.

In Sections 1.2 and 1.3 below, we shall review the background to this method with special emphasis on aspects which are important for the analysis of X-ray satellite and related spectra. An analysis of  $n'snp^5$ -configurations and of K-hypersatellite transitions<sup>11</sup>, which is expected to provide a stringent test of the MCDF method<sup>12</sup>, is presented as an example in Sections 1.4 and 1.5.

Many recent works<sup>13-21</sup> which deal with the influence of relativistic and quantum-electrodynamical effects on binding and X-ray transition energies in heavy atoms are based on Dirac-Fock (DF) calculations. They are either single-configuration or configuration average calculations, as are the calculations of binding energies by Huang et al.<sup>22</sup> and of Coster-Kronig energies by Chen et al.<sup>23</sup>. In the latter works, Dirac-Slater (DS) wave functions have been used as approximations of the DF wave functions.

As far as we know, there is only one calculation of X-ray transitions rates in the DF scheme, namely, that of Scofield<sup>24</sup>. A few works analyse the level structure or transitions in open-shell systems using the MCDF method. Among these the works of Kim and Desclaux<sup>25</sup> and Armstrong et al.<sup>26</sup> deal with few-electron ions, whereas Desclaux and Kim<sup>27</sup>, Grant et al.<sup>28</sup> and Rose et al.<sup>29,30</sup> treat outer open shells

in heavy atoms. In the case of inner-shell transitions, there is the MCDF analysis of KLL-Auger transitions by Briancon and Desclaux<sup>31</sup>, and of KK-KL-hypersatellite transitions by Suvanen and Åberg<sup>32</sup> and Schreckenbach et al.<sup>33</sup>. In Section 1.4 we shall relate these works to the relativistic intermediate-coupling analysis of KLL-Auger energies by Asaad and Petrini<sup>34</sup>, and to Larkins' approach<sup>35</sup> for obtaining relativistic LS-term energies. Although we shall concentrate on the MCDF method, we would also like to mention the relativistic random-phase approximation (RPA)<sup>37</sup> and the  $1/Z$ -expansion<sup>38,39</sup> methods as possible complementary tools for the treatment of X-ray satellite spectra.

## 1.2 THE PHOTON-ELECTRON AND ELECTRON-ELECTRON INTERACTION

Since the lack of a proper treatment of the electron-electron interaction is the main obstacle to the development of a consistent relativistic invariant many-electron theory, we shall begin with a brief overview of the quantum-electrodynamical approach<sup>40</sup> which leads to the Breit interaction in addition to the Coulomb interaction. Since these interactions are consequences of the exchange of virtual photons from the point of QED, we need, in addition to Dirac's central-field equation of a single electron, Maxwell's equations in the covariant form. This also enables us to introduce the concept of the relativistic radiative transition probability.

For that purpose we introduce the four-dimensional space defined by

$x = (x_1, x_2, x_3, x_4) = (x, y, z, ict)$ . We define two four-vectors in that space, namely,  $A = (A_x, A_y, A_z, i\phi/c)$  and  $j = (j_x, j_y, j_z, c\rho)$ , as combinations of the vector and scalar potentials and of the current and the charge density, respectively. The components of  $A$  fulfil the wave equation

$$\square A_\mu = \sum_{\mu=1}^4 \frac{\partial^2 A_\mu}{\partial x_\mu^2} = -\mu_0 j_\mu \quad (\mu = 1, 2, 3, 4), \quad (1.1)$$

which has this form provided that the Lorentz condition

$$\sum_{\mu=1}^4 \frac{\partial A_{\mu}}{\partial x_{\mu}} = 0 \quad (1.2)$$

is fulfilled. Equations (1.1) and (1.2) are invariant and the field vectors remain unaltered in any gauge transformation

$$A'_{\mu} = A_{\mu} + \frac{\partial \Lambda}{\partial x_{\mu}} \quad (1.3)$$

where  $\Lambda$  fulfils the equation

$$\square \Lambda = 0 \quad (1.4)$$

but is otherwise arbitrary. In the free-field space the solution of equation (1.1) can be obtained in terms of plane waves. If the electromagnetic field is closed in a normalisation box of volume  $\Omega$  and the quantisation rules are applied to the plane-wave expansion coefficients after an appropriate generalisation (e.g. Ref. 40, Section 16) of condition (1.2), then the Lorentz-invariant vector potential operators

$$A_{\mu}(\mathbf{x}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{k}, \lambda} \sqrt{\frac{\hbar}{2\epsilon_0 \omega}} e^{(\lambda)}_{\mu} \left[ c_{\mathbf{k}, \lambda} e^{i\mathbf{k}\mathbf{x}} + c_{\mathbf{k}, \lambda}^{\dagger} e^{-i\mathbf{k}\mathbf{x}} \right]_{\mu=1, 2, 3, 4} \quad (1.5)$$

are obtained. Here  $\mathbf{k}\mathbf{x}$  is the scalar product of the four-vector  $\mathbf{x}$  and the four-dimensional propagation vector  $\mathbf{k} = (\vec{k}, i\omega/c)$  which satisfies the condition  $k^2 = |\vec{k}|^2 = \omega^2/c^2$ . The operators  $c_{\mathbf{k}, \lambda}$  and  $c_{\mathbf{k}, \lambda}^{\dagger}$  are the photon annihilation and creation operators, respectively. The four-vectors  $e^{(\lambda)}$  are the polarisation unit vectors fulfilling the orthogonality relations  $e^{(\lambda)}_{\mu} e^{(\lambda')}_{\nu} = \delta_{\lambda\lambda'}$ , and  $e^{(\lambda)}_{\mu} e^{(\lambda)}_{\nu} = \delta_{\mu\nu}$ . Two of them ( $\lambda = 1, 2$ ) can be chosen orthogonal to  $\vec{k}$  and one parallel to  $\vec{k}$  ( $\lambda = 3$ ). It follows, in accordance with the orthogonality relations, that  $e^{(\lambda)}_{\mathbf{k}} = 0$  ( $\lambda = 1, 2$ ) (transverse photons) and  $e^{(3)}_{\mathbf{k}} = \omega/c$  (longitudinal photons). The fourth vector for which  $e^{(4)}_{\mathbf{k}} = i\omega/c$  corresponds to the scalar photons which are actually responsible for the Coulomb interaction.

Having briefly established the properties of the electromagnetic field, we also

need to consider Dirac's equation of an electron moving in an external field.

Suppose that this field is represented by the vector potential  $A = (A_x, A_y, A_z, i\phi c)$ .

Then Dirac's equation which is satisfied by the four-spinor

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \quad (1.6)$$

is given by

$$[ic\gamma + ice\gamma + mc^2]\psi = 0 \quad (1.7)$$

where the components of  $p$  are the operator  $-i\hbar \frac{\partial}{\partial x_\mu} l$  ( $\mu = 1, \dots, 4$ ) and where  $e$  is the absolute value of the charge of the electron. Each component of

$\gamma = (\gamma_1, \gamma_2, \gamma_3, \gamma_4)$  is a  $4 \times 4$  matrix defined below and  $l$  is the  $4 \times 4$  unit matrix.

The matrices  $\gamma$  are related to the  $2 \times 2$  Pauli matrices  $\sigma_x, \sigma_y, \sigma_z$  (e.g. Ref. 40, p.73) and the unit  $2 \times 2$  matrix  $l$  by

$$\gamma_\mu = -i\beta\alpha_\mu \quad (\mu = 1, 2, 3): \quad \gamma_4 = \beta \quad (1.8)$$

where

$$\alpha_\mu = \begin{pmatrix} 0 & \sigma_\mu \\ \sigma_\mu & 0 \end{pmatrix} \quad (\mu = 1, 2, 3) \quad \text{and} \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (1.9)$$

In the absence of the photon field (1.5) but in the presence of a local central field  $V(r)$  for which  $A = (0, 0, 0, i\frac{V(r)}{c})$ , we obtained from equation (1.7) by the substitution  $\psi \rightarrow \psi e^{-i\epsilon t/\hbar}$  Dirac's stationary-state central-field equation

$$H_D \psi_{\kappa m} = (c\bar{\alpha} \cdot \bar{p} + mc^2\beta - eV(r)l)\psi_{\kappa m} = \epsilon \psi_{\kappa m} \quad (1.10)$$

where the Dirac operator  $H_D$  commutes with  $j^2 = (\bar{l} + \bar{s})^2$ ,  $j_z$  and the permutation operator  $p$  which are all represented by  $4 \times 4$  operator matrices. In particular,



the spin is represented by the matrix operator

$$\vec{s} = \frac{\hbar}{2} \vec{\sigma}' = \frac{\hbar}{2} \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix} \quad (1.11)$$

where  $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$  is the Pauli matrix in the vector form, and the operator by the matrix operator

$$p = \beta P, \quad (1.12)$$

where  $P$  is the ordinary permutation operator. However, instead of the operator (1.12) the eigenvalues of another commuting operator, namely,  $K = \beta[1 + \vec{\sigma}' \cdot \vec{L}]$ , is used to classify the solutions of Dirac's central-field equation. As shown in many textbooks, (e.g. Ref. 41) the solutions can be written in terms of the Dirac central field four-spinors

$$\psi_{\kappa m} = \begin{bmatrix} R_{+1}(r) \langle \theta \Phi; \zeta | j - \frac{1}{2} a, j, m \rangle \\ i R_{-1}(r) \langle \theta \Phi; \zeta | j + \frac{1}{2} a, j, m \rangle \end{bmatrix} \quad (1.13)$$

where  $R_{+1}$  and  $R_{-1}$  are the large and small radial components, respectively, and where the spin-orbit eigenfunctions

$$\langle \theta \Phi; \zeta | \lambda, j, m \rangle = \sum_{\mu} Y_{\ell}^{m-\mu}(\theta, \Phi) \phi^{\mu}(\zeta) (\ell, 1/2, m-\mu, \mu | j, m) \quad (1.14)$$

are superpositions of the Pauli two-spinors  $\phi^{1/2} = \begin{pmatrix} \delta_{\zeta, 1/2} \\ 0 \end{pmatrix}$  and  $\phi^{-1/2} = \begin{pmatrix} 0 \\ \delta_{\zeta, 1/2} \end{pmatrix}$ .

In the eigenfunction (1.14)  $\lambda = j - \frac{1}{2} a \beta$ , where  $\beta = \pm 1$  labels the rows in the wave function (1.13) and  $a = \pm 1$  distinguishes between the two possible couplings of spin and angular momenta in  $j = \ell + \frac{1}{2} a$ . Since  $K \psi_{\kappa m} = -\kappa \psi_{\kappa m}$ , where  $\kappa = \ell$  for  $j = \ell - \frac{1}{2}$  and  $-(\ell+1)$  for  $j = \ell + \frac{1}{2}$ ,  $\kappa$  is connected to  $a$  by  $\kappa = -(j + \frac{1}{2}) a$ . It can also be shown that

$$p \psi_{\kappa m} = (-1)^{\ell} \psi_{\kappa m} \quad (1.15)$$