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Statistical analysis of the $(3d+4s)^5 4p$ spectrum of Cr I

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Statistical properties of the energy levels derived from the $(3d+4s)^5 4p$ spectrum of Cr I have been investigated. The hypothesis that the density distribution of the energy levels is of the Gram-Charlier type has been rejected by a χ^2 test. On the other hand, in sequences of the energy levels corresponding to fixed values of the total angular momentum J, the energy-level densities are shown to be Gaussian. In the fixed-J sequences, spacings between neighboring levels are Poisson-like. The low-order energy moments have been used to approximate the $(3d+4s)^5 4p$ energy-level spectrum. The secular behavior and fluctuations of this spectrum are discussed.

I. INTRODUCTION

The complex nature of many-electron systems has caused more than half a century of work on their satisfactory theoretical description by many scientific groups. In spite of considerable methodological progress and a large increase in applications of quantum-mechanical calculations due to the computer revolution, many experimental results remain out of reach for numerical methods of modern theories of many-electron systems. For this reason new methods are still needed. Among many procedures being developed now, the statistical methods for the description of spectra of complex many-electron systems are of particular interest. These methods were first proposed in the theory of the atomic nucleus in the thirties. For reviews of this subject see French and Kota [1] and Brody *et al.* [2] where further references may also be found.

The reasons that one resorts to statistical concepts for the study of many-particle microscopic systems are manifold. First, detailed properties of the spectrum are frequently not really open to calculations, e.g., the Hamiltonian is not known or its eigenvalues cannot be calculated accurately enough. Second, considerations essentially different from the study of individual levels may reveal new features of the system, which can be obscured by detailed calculations of the energy levels. Third, statistical concepts create a possibility of solving old problems using new approaches as, for example, approximating real spectra by the ones derived from the spectral-density-distribution moments [2].

The first papers devoted to statistical properties of atomic spectra were published 30 years ago by Rosenzweig and Porter [3] and by Trees [4]. The authors studied energy-level-spacing distributions. They showed that the nearest-neighbor spacings in sequences of levels corresponding to the same set of quantum numbers follow the Wigner distribution, while in the case of mixed sequences the spacing distribution is exponential. Empirical studies on the nature of level density arising from a definite configuration (partial level density) in several atomic configurations by Parikh [5] and by Cowan [6] showed that the level density behaves in a Gaussian-like fashion. More detailed analysis by the present authors [7] resulted in the conclusion that the distribution is nearly Gaussian, but only if levels with the same total-angular-momentum quantum number J are considered.

The first step in the mathematical study of an unknown statistical distribution is the calculation of its moments. Compact formulas for the second-order moments (variances) in the study of the distribution of level and line energies were established for the most general electronic configurations by Bauche-Arnoult, Bauche, and Klapish [8] and Bauche and Bauche-Arnoult [9]. The same authors implemented these formulas to interpret several atomic spectra. The first two moments of the distribution of the eigenvalues of a Hamiltonian in an N-electron spin-adapted model space were derived by the present authors [10]. The spectral distribution function derived from the moments contains the statistical information about the spectrum. This information may be used in a way complementary to the way in which, in the conventional spectroscopy, information is derived from diagonalization of the Hamiltonian matrix. Usually, in the statistical spectroscopy, one sets different problems than in the conventional one. The statistical approach is best suited to study general behavior of spectra, while the conventional one is best suited to determine properties of individual energy levels. Nevertheless, one may apply the statistical approach even to study structure details of spectra. For example, the spectral distribution function was successfully applied to approximate the real nuclear [11], atomic [12], and model Hamiltonian [13] spectra. The state of the art in the field of statistical theories of atomic spectra has been recently reviewed by Bauche and Bauche-Arnoult [14].

In this paper we study statistical properties of the Cr I $(3d+4s)^5 4p$ energy-level spectrum. The energy values have been taken from a parametric least-squares fit to the experimental spectrum [15]. We show that the distribution of energy levels with the same total-angular-momentum quantum number is nearly Gaussian. In fact, it is a low-moment Gram-Charlier distribution with a predominant Gaussian component. We calculate the values of the spectral moments from the real (fitted) spectrum. Finally, we compare the smoothed spectra, derived from the low-moment distribution functions, with the real ones, showing that differences between the smoothed and the real spectra (fluctuations) behave similarly to nuclear [2] and to model-Hamiltonian [13] spectra. As an additional result of the present calculations we obtain the nearest-neighbor energy-level-spacings distribution for the analyzed spectrum. Spacings of the nearest-neighbor levels of the same total-angular-momentum quantum number behave in a Poisson-like way, showing the existence of approximate constants of motion (the total spin and the total orbital angular momentum).

II. STATISTICAL DESCRIPTION OF THE HAMILTONIAN SPECTRA

The density $\tilde{\rho}(E)$ of the discrete spectrum $E_1, E_2, \ldots, E_D$ is represented by the discrete normalized frequency function

$$\tilde{\rho}(E)=D^{-1}\sum_{i=1}^{D}\delta(E-E_i)\ , \qquad (1)$$

$$\int_{-\infty}^{+\infty}\tilde{\rho}(E)dE=1\ , \qquad (2)$$

and the corresponding average energy $\bar{E}$ and the moments M_q are

$$\bar{E}=\int_{-\infty}^{+\infty}E\tilde{\rho}(E)dE\ , \qquad (3)$$

$$M_q=\int_{-\infty}^{+\infty}(E-\bar{E})^q\tilde{\rho}(E)dE\ . \qquad (4)$$

The normalized distribution function $\tilde{F}(E)$ is obtained by integrating the frequency function

$$\tilde{F}(E)=\int_{-\infty}^{E}\tilde{\rho}(E')dE'\ . \qquad (5)$$

If the distribution moments are known, the discrete frequency function may be approximated by a continuous frequency function $\rho(E)$ chosen so that a given number of the lowest moments calculated with either function are the same.

Since eigenvalues of the N-electron Hamiltonians in finite-dimensional spaces tend to be distributed in a Gaussian-like fashion [5–7,13,14], we take the Gaussian function as a starting point and then modify it in order to consider the higher moments of the distribution. It is convenient to construct the continuous frequency function $\rho(E)$ in terms of the dimensionless variable

$$x=(E-\bar{E})/\sigma\ , \qquad (6)$$

where $\sigma=M_2^{1/2}$ is the width (dispersion) of the spectrum. The frequency function may then be expanded in terms of Hermite polynomials [16]

$$\rho(x)=(2\pi)^{-1/2}e^{-x^2/2}\sum_j c_jH_j(x)\ , \qquad (7)$$

where, by the orthogonality relationship for Hermite polynomials, the coefficients are given by

$$c_j=\frac{1}{j!}\int_{-\infty}^{+\infty}H_j(x)\rho(x)dx\ . \qquad (8)$$

Taking into account that $M_k=\int_{-\infty}^{+\infty}x^k\rho(x)dx$, c_j may be expressed as a linear combination of M_k with $k\le j$. The resulting equation is known as the Gram-Charlier expansion [16]. If the series (7) is terminated after p terms, then

$$\int_{-\infty}^{+\infty}(E-\bar{E})^q[\tilde{\rho}(E)-\rho(E)]dE=0 \qquad (9)$$

for $q=0,1,\ldots,p$. In such a case the continuous function ρ is referred to as the p-moment equivalent of $\tilde{\rho}$.

The χ^2 test is used as a measure of the quality of the p-moment approximation to the frequency function. The value of χ^2 is calculated in the following way. First, the Hamiltonian spectrum is normalized to the distribution with $\bar{E}=0$ (subtracting $\bar{E}$ from all energy levels) and $\sigma=1$ (dividing $E_i-\bar{E}$ by σ). Then the energy range is divided into r intervals $(-\infty,x_1),(x_1,x_2),\ldots,(x_{r-1},+\infty)$ in such a way that

$$F_G(x_{k+1})-F_G(x_k)=D/r\ , \qquad (10)$$

where $F_G(x)$ corresponds to the standard Gaussian fre-

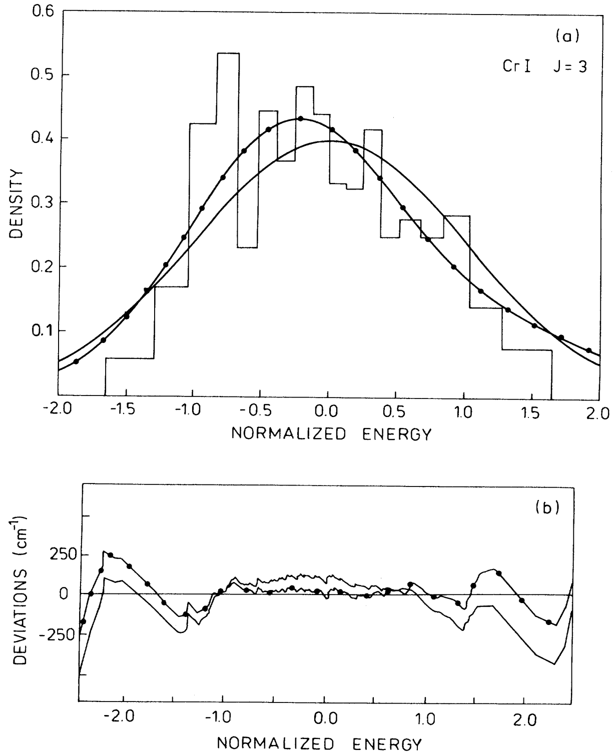

FIG. 1. (a) The histogram of the exact density of $(3d+4s)^5 4p$, $J=3$, spectrum of Cr I compared to two- (——) and seven-moment (–·–·–·–) Gram-Charlier expansions. The two-moment Gram-Charlier expansion corresponds to the Gaussian distribution. The energies are normalized according to Eq. (6). (b) The level-to-level deviations between the real spectrum and its Gaussian and seven-moment representations.

quency function. If $\tilde{n}_k$ is the number of the Hamiltonian eigenvalues within the interval (x_k, x_{k+1}), and

$$n_k = F(x_{k+1}) - F(x_k) , \tag{11}$$

where

$$F(x) = \int_{-\infty}^{x} \rho(x')dx' , \tag{12}$$

then

$$\chi^2 = \sum_{k=1}^{r} (\tilde{n}_k - n_k)^2 / n_k . \tag{13}$$

The value of χ^2 is then compared with a critical value χ^2_{crit} chosen to correspond to the 5% probability level [17].

If $F(x)$ is a continuous distribution function, the corresponding smoothed spectrum can be defined as the set of values x_i which satisfies

$$F(x_i) = (i - \tfrac{1}{2})/D \tag{14}$$

for $i = 1, 2, \ldots, D$ [11–13]. A comparison of the real energy levels and those derived from the distribution function according to Eq. (14) leads to the notions of the secular eigenvalue density and of fluctuations [2]. The secular density is defined by several moments. If it is described correctly, the fluctuations are small, energy independent, and insensitive to increasing the value of p.

The final quantity being studied is the spacing between adjacent eigenvalues. As is known [3,7,18], the spacings between eigenvalues belonging to the same symmetry species are distributed according to the Wigner distribution law

$$W(d) = \frac{\pi}{2} d \exp(-\pi d^2/4) , \tag{15}$$

where $d = s/\bar{s}$, s is the spacing and $\bar{s}$ is the mean value of s. The eigenvalues of different symmetries are not correlated and, in consequence, a superposition of several sets of different symmetry eigenvalues leads to an exponential

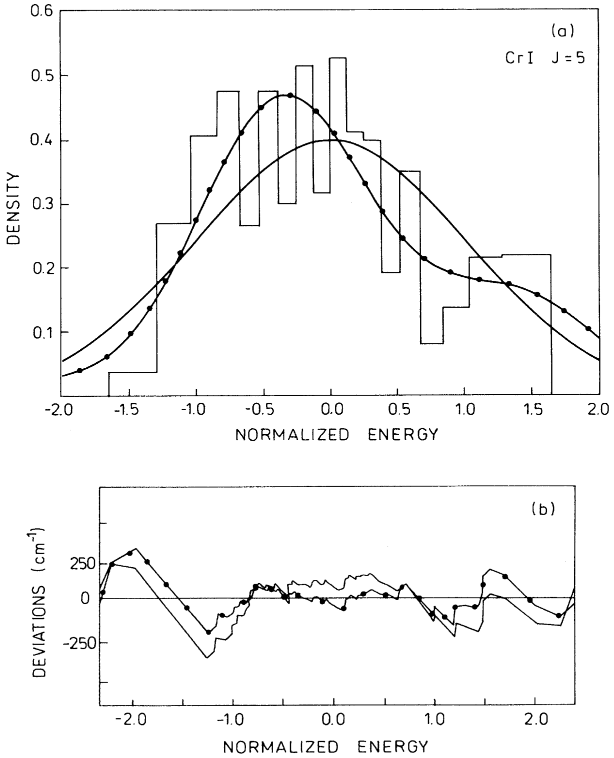

FIG. 2. (a) The histogram of the exact density of $(3d+4s)^5 4p$, $J=5$, spectrum of Cr I compared to two- (———) and nine-moment (–·–·–·–) Gram-Charlier expansions. (b) The level-to-level deviations between the real spectrum and its Gaussian and nine-moment representations.

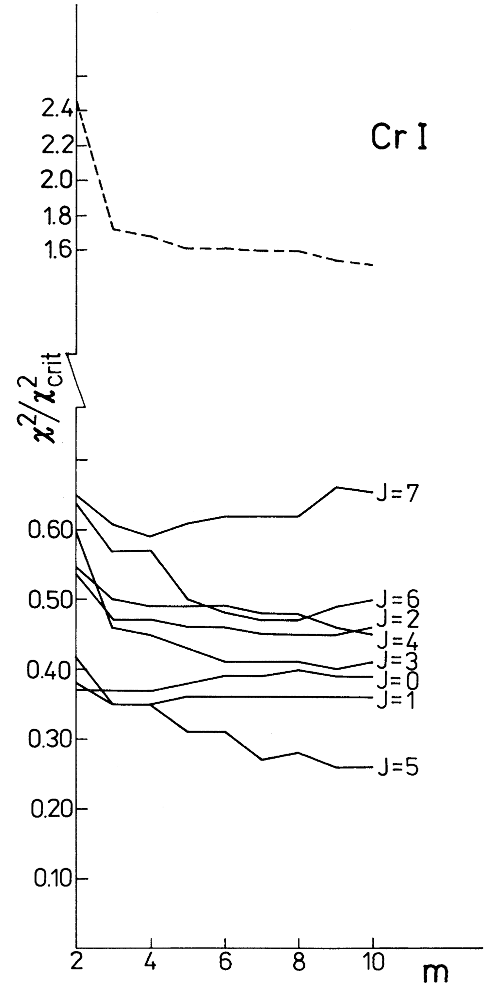

FIG. 3. The ratio of the calculated to the critical (for the 5% probability level) values of χ^2 for testing the Gram-Charlier secular density hypothesis vs the highest moment m taken into account in the Gram-Charlier expansion. The solid lines represent the cases of sequences of energy levels of the same J and the dashed line represents the case of sequence of all $(3d+4s)^5 4p$ energy levels.

distribution of the spacings

$$X(d)=\exp(-d)\ . \qquad (16)$$

These rules may be used to study approximate (or hidden) symmetries [3]. If, beyond the symmetries considered explicitly, there exists another one, then the spacing distribution remains exponential or it is an intermediate between the Wigner and the exponential one.

III. RESULTS AND DISCUSSION

A detailed study has been performed for the $(3d+4s)^5 4p$ spectrum of Cr I. Energy values are assumed to be the same as the ones obtained from the parametric least-squares fit to the experimental spectrum [15]. The $(3d+4s)^5 4p$ configurations comprise 684 energy levels and the residual mean-square deviation of this fitting is 183 cm^{-1}. Histograms of the empirical density of energy levels are shown in Fig. 1(a) (145 energy levels corresponding to $J=3$) and in Fig. 2(a) (76 energy levels corresponding to $J=5$). The level densities first increase to a maximum somewhere near the average energy and then fall off to zero at the upper limit. These histograms were

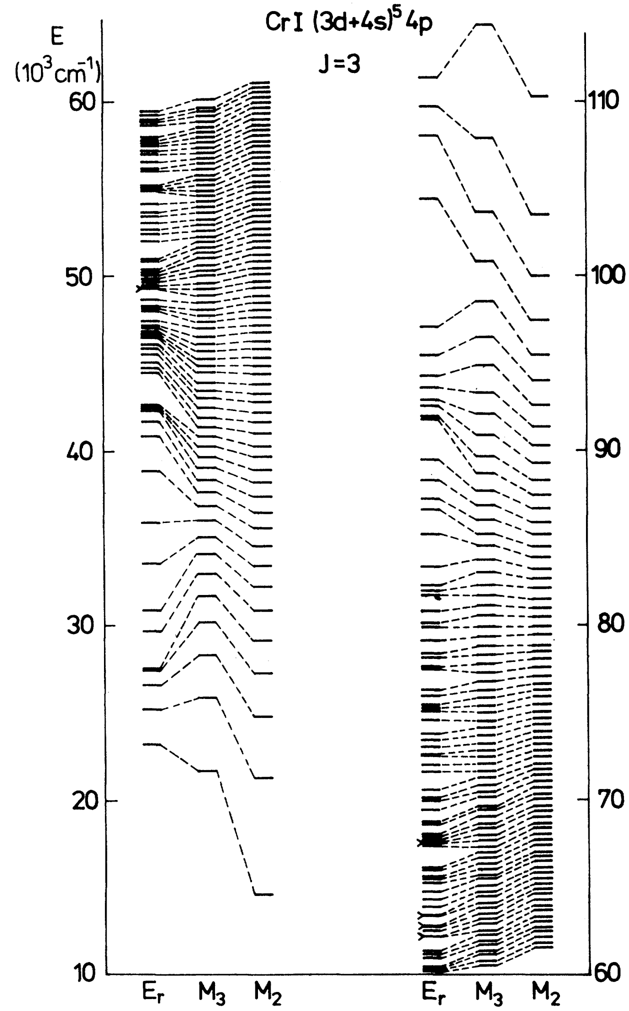

FIG. 4. The real $(3d+4s)^5 4p$, $J=3$, spectrum of Cr I (E_r) compared to its n-moment-generated counterparts (M_n).

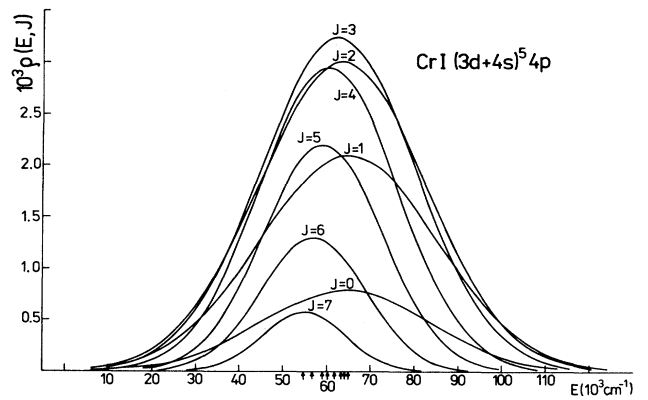

FIG. 5. The Gaussian density functions representing the secular densities of energy levels in the $(3d+4s)^5 4p$ spectrum of Cr I. Arrows indicate the average energies for given J values.

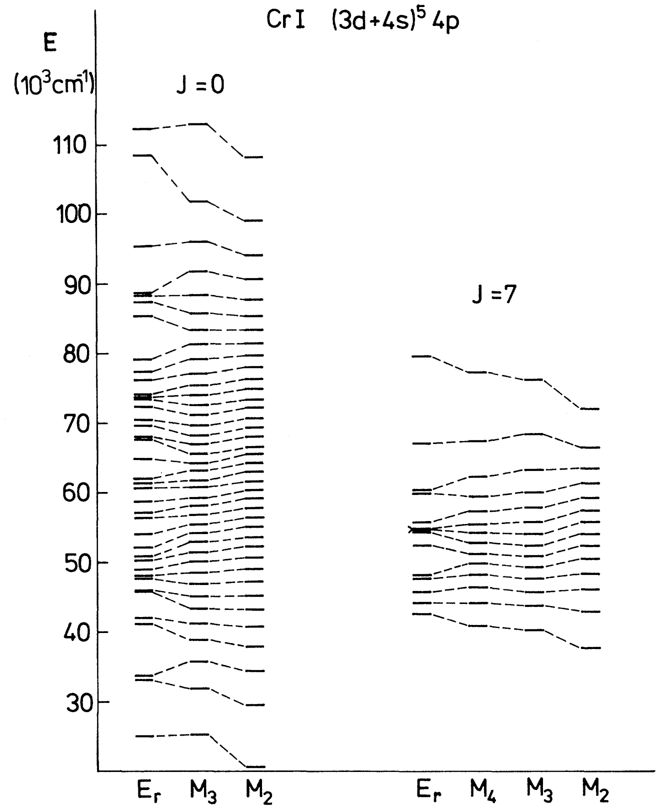

FIG. 6. The real $(3d+4s)^5 4p$, $J=0$ and $J=7$, spectra of Cr I (E_r) compared to their n-moment-generated counterparts (M_n).

compared to Gaussian and low-moment frequency functions. Let us note that the energy intervals in the histograms have been defined according to Eq. (10) and therefore their width varies with energy. Hypotheses concerning the character of the energy-level density functions have been tested using the χ^2 test. The ratios $\chi^2/\chi^2_{\mathrm{crit}}$ for subsets of energy levels of the fixed total-angular-momentum quantum number ($J=0,1,2,3,4,5,6,7$) are plotted versus the length of the Gram-Charlier expansion in Fig. 3. In all cases the hypothesis that the distribution is Gaussian is accepted. Taking beyond-Gaussian terms reduces the χ^2 value. This reflects the fact that the exact distribution of the energy levels is asymmetric. However, making the expansions longer than a certain limit does not improve the fitting. On the other hand, the density of all the energy levels, disregarding their symmetry, is not Gaussian. The resulting ratio $\chi^2/\chi^2_{\mathrm{crit}}$ is also plotted in Fig. 3. These observations are consistent with our earlier findings for atomic [7] and for a model Hamiltonian [13] spectra. Density functions accepted by the χ^2 test as Gaussian for sequences of fixed-J energy levels were plotted in Fig. 4 to show the global shape of the spectrum considered. The density functions for different fixed-J values strongly overlap. As a result, there is a high cumulative density of energy levels in the central region of the spectrum. It reflects the very complicated structure of the spectrum of complex atomic configurations.

In Figs. 5–7, spectra derived from the n-moment distribution functions according to Eq. (14) are compared to the real spectra. In Figs. 5 and 6 the real energy levels of $J=0,3,7$ and the corresponding energy levels generated by the n-moment distribution functions are shown. The overall structure of the smoothed (moment-generated) spectra agrees well with that of the real spectra. The moment-generated spectra reproduce the real spectra especially well in their central parts. The discrepancies in the areas of the lowest and highest eigenvalues are reduced if the number of moments taken into account increases. Fluctuations, i.e., the deviations of the moment-generated spectra from the real ones, decrease when the lengths of the corresponding expansions increase [Figs. 1(b) and 2(b)]. The number of $(3d+4s)^5 4p$ energy levels is sufficiently large to allow considering also the sets of the energy levels with the same total, orbital, and spin angular momentum quantum numbers as statistical ensembles. The real $^3F_2$ and $^3P_0$ energy levels as well as their moment-generated counterparts are displayed in Fig. 7.

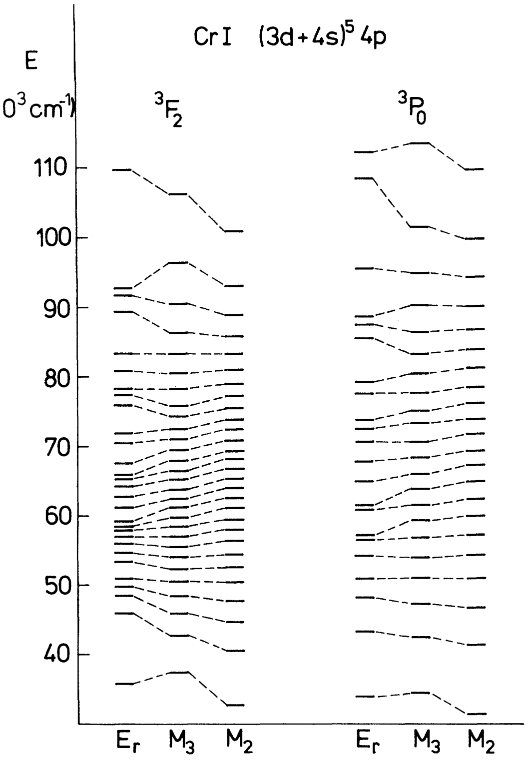

FIG. 7. The real $(3d+4s)^5 4p$, $^3F_2$ and $^3P_0$, spectra of Cr I (E_r) compared to their n-moment-generated counterparts (M_n).

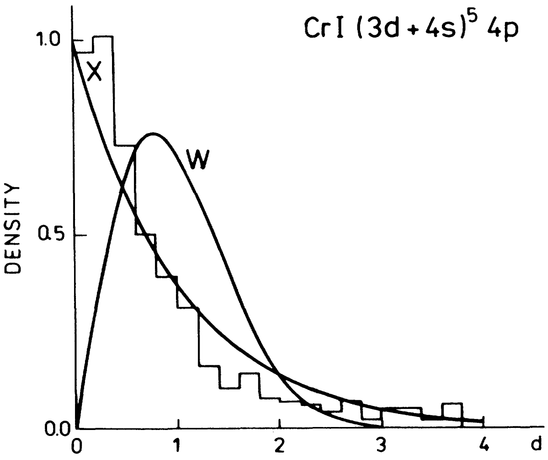

FIG. 8. The exact distribution of the adjacent level spacings derived from the $(3d+4s)^5 4p$ spectrum of Cr I compared to the Wigner (W) and to the Poisson (X) laws. In order to obtain the exact distribution, separate histograms for each J were constructed and then combined.

An analysis of the adjacent level-spacing distributions confirms earlier results obtained for nuclear [2], atomic [3,7], and model Hamiltonian [18] spectra. The histogram of the spacings displayed in Fig. 8 is plotted for fixed-J sequences of energy levels. The spacing distribution is clearly not of the Wigner type. In the considered atom the orbital- and spin-angular-momentum operators nearly commute with the Hamiltonian. Then, they describe approximate, but neglected in this analysis, symmetries. Energy levels belonging to a given J, but differing by the L, and S quantum numbers are almost noncorrelated in their positions. Therefore, each J sequence of the energy levels is a superposition of many unrelated sequences, giving rise to many very close spacings and leading to an exponential-like distribution. The departure from the Wigner distribution should be greater the smaller the spin-orbit interaction.

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