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Variance of the distributions of energy levels and of the transition arrays in atomic spectra

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Formulas are derived for the mean values and variances of the energy distributions of the levels of an atomic configuration and of the radiative transitions between the levels of two configurations (in intermediate coupling). The variance σ^2 of the distribution of the eigenstate energies belonging to a given configuration is considered first: σ^2 is expressed as a linear combination of squares and cross products of the usual Slater electrostatic and spin-orbit radial integrals. It is shown how this expression can be used to check the numerical matrices of energy-integral coefficients. Then expressions are derived for the mean value and for the variance of the weighted distribution of the transition energies between two configurations (the weight of each transition being its strength) in the $nl^{N+1} - nl^N n'l'$ and $nl^N n'l' - nl^N n''l''$ cases. This derivation is based on the second-quantization formalism. An extension is made to the case of complementary configurations. For transitions $nl^{N+1} - nl^N n'l'$, an explicit formula is obtained for the shift between the mean energy of the transition array and the difference of the mean energies of the configurations. Numerical tables of the angular coefficients appearing in σ^2 are given for most cases where l, l', $l'' \leq 3$. The main application presented here concerns highly ionized spectra of molybdenum, with transitions between $3d^{N+1}$ and $3d^N 4p$, $3d^N 4f$, $3d^N 5p$, and $3d^N 5f$. The agreement between experimental and theoretical (*ab initio*) mean wave numbers and variances is good. A discussion of the physical conditions of applicability of the results to experimental situations is given.

I. INTRODUCTION

In the past few years, the spectroscopy of highly ionized atoms has gathered large momentum mainly from two factors: the research in thermonuclear plasmas and the development of x-ray astrophysics. Quite often, it happens that ground configurations of these atoms possess many equivalent electrons, e.g., $3d^N$ for Mo XV–Mo XXIV[1-3] and for Sn XXIII-Sn XXXII,[4] $4d^N$ for W XXXI-W XXXV[5] and $4f^N$ for W XVIII-W XXVIII.[6] The important transitions of these atoms, which belong to the types l^{N+1}-$l^N l'$ and $l^N l'$-$l^N l''$, appear in the range 5–150 Å. In all of these cases, the width of the transition array is much smaller than the mean wavelength. Apart from some exceptions (e.g., in the $2p^N$ configurations of Fe XVIII-Fe XXII and the like[7]) it is impossible to resolve the numerous individual lines and therefore the spectra show characteristic "bands," each of which originates in a different ionization stage and pair of configurations. It must be stressed that although the individual lines are merged together by various line-broadening mechanisms (such as instrumental width, Doppler effect, Stark broadening, etc.), the spectral widths of these bands owe very little to these effects and come essentially from the spread in energy of configurations and transition arrays. The existence of these bands made hardly possible the interpretation of the spectra, and even the identification of the ionization stages, classically based on the classification of individual lines. As a consequence of this lack of means of interpretation, there is a large amount of unpublished material.

The present work is concerned with the description of the bands as such, i.e., as statistical entities characterized by their first two moments, namely, their mean wavelengths and spectral widths. Previous work on this question is scarce. Important numerical studies have been carried out by Cowan.[8,9] Concerning formal theories, Moszkowski[10] treated the problem of the widths of transition arrays with simplifying assumptions. He also obtained the width of the $(nl)^N$ configuration, for which Layzer[11] gave later an elegant derivation. In the present work we expose, in greater detail than in a short previous article,[12] the methods and the formal and numerical results involving all the relevant radial (Slater and spin-orbit) integrals. This description, although initiated by the necessity of interpreting highly ionized spectra, is however more general and could be useful in any event when one wishes to refer to transitions between two configurations as a whole. For instance, in the case of ordinary x-rays, it allows to take into account the coupling of the hole in the deep shell with the external open-shell electrons. This could be a means of explaining some recent high-resolution x-ray measurements[13,14] and perhaps of evaluating the effect of the solid on the emitting atom. Also, in the classical spectroscopic studies of very complex spectra (lanthanides, actinides), it can provide a help for evaluating the spectral range of a transition array.

In the following, we first describe which theoretical model we have considered for computing the expressions for the first and second moments of the distributions of states in an arbitrary configuration. Then, we present the calculations concerning the transition arrays in the cases l^{N+1}-$l^N l'$ and $l^N l'$-$l^N l''$, for which we give analytical formulas, both for the mean wave number and for the spectral width. These formulas are tabulated to allow quick computations in the most common cases. Finally, we describe in some detail the application to the spectra of highly ionized molybdenum Mo XV–Mo XXIV, where we computed the transitions $3d^{N+1}$-$3d^N nl$, with N running from 0 to 9 and nl being $4p$, $4f$, $5p$, and $5f$, and compared the results with experiment.

II. STATISTICAL WIDTH OF A CONFIGURATION

The standard deviation of the state-energy distribution in a configuration is the square root of the variance

$$\sigma^2=(\langle\varphi_i|H|\varphi_i\rangle^2)_{\mathrm{av}}-(\langle\varphi_i|H|\varphi_i\rangle_{\mathrm{av}})^2\,, \qquad (1)$$

i.e., of the average value of the squares of the energies of the *eigenstates* φ_i minus the square of the average value of these energies. The only part of the nonrelativistic Hamiltonian H which is relevant here is the sum of the electrostatic and spin-orbit operators G and Λ: hence we use

$$H=G+\Lambda=\sum_{i>j=1}^{N}\frac{e^2}{r_{ij}}+\sum_{i=1}^{N}\xi(r_i)\vec{s}_i\cdot\vec{l}_i\,.$$

For real Hermitian matrices, it is well known that the following quantities are invariant under any orthogonal transformation: (i) the sum of the diagonal elements (the trace) and (ii) the sum of the squares of all the elements. Using these properties Eq. (1) can be written

$$\sigma^2=\frac{1}{g}\sum_{i,j=1}^{g}(\langle\psi_i|H|\psi_j\rangle)^2-\left(\frac{1}{g}\sum_{i=1}^{g}\langle\psi_i|H|\psi_i\rangle\right)^2\,, \qquad (2)$$

where the sum indices run over the g *basis states* of the configuration in any coupling scheme.

For the part of σ^2 purely due to the spin-orbit operator, the convenient coupling scheme is pure j-j coupling. The matrix elements are easily written and the summations carried out directly.

For the purely electrostatic part of σ^2, the convenient basis scheme is that of Slater determinants. The method used for writing the matrix elements is that described by Condon and Shortley,[15] except for the replacement of their numerical coefficients (pp. 178 and 179 in Ref. 15) through the use of formal $3j$ coefficients.

The part of σ^2 resulting from products of electrostatic and spin-orbit matrix elements vanishes. This fact can be understood without calculation. Consider a coupling where the electrostatic operator is strictly diagonal (the corresponding eigenstates, denoted $|\psi\rangle=|\alpha SLJM\rangle$, would generally be obtained through a diagonalization). Products of any electrostatic (Slater) radial integral R^k and of any spin-orbit integral ζ have a null coefficient in both sums of Eq. (2): on one hand, in the second sum, all ζ's are absent from the trace, due to the Landé center-of-gravity rule in any Russell-Saunders (RS) term; on the other hand, in the first sum, any product $R^k\zeta$ only appears in the squares $\langle\psi_i|H|\psi_i\rangle^2$ of the diagonal elements and its coefficients, for all the states $|\psi_i\rangle$ of a given RS term, are a constant times the relevant coefficient of ζ: again the center-of-gravity rule shows that their sum is zero.

A. nl^N configurations

In the case of an nl^N configuration, the σ^2 expression would in principle contain three types of squares and cross products of the Slater integrals $F^k\equiv F^k(nl,nl)$ and of the spin-orbit radial integral

$$\zeta\equiv\zeta_{nl}=\int_0^\infty|R_{nl}(r)|^2\xi(r)dr\,,$$

namely, $F^kF^{k'}$, $F^k\zeta$, and ζ^2. But in fact (i) the contributions of the $F^k\zeta$ type vanish (see above); (ii) we have extended the Hamiltonian to take into account the second-order energy effect $\alpha L(L+1)$, first proposed by Trees,[16] which is frequently introduced in the parametric studies of intermediate coupling because of its numerical importance.

For these reasons, the result for σ^2 is presented in Table I(a) as the sum of four contributions:

$$\sigma^2=D_1+D_2+D_3+D_4\,, \qquad (3)$$

where D_1–D_4 correspond, respectively, to the radial parts $F^kF^{k'}$, αF^k, α^2, and ζ^2.

Parts D_1–D_3 have the same dependence on N, namely,

$$N(N-1)(4l-N+1)(4l-N+2)\,,$$

a result which has already been suggested for two-electron interaction effects by Moszkowski[10] and later demonstrated by Layzer.[11] As concerns the parts in α (D_2 and D_3), this is not surprising because Tree's operator, $\alpha(\vec{L})^2$, is, within an additive constant, a two-electron operator.

Other second-order electrostatic effects on the energy levels, due to far-configuration mixing, correspond to operators of the type $F^k\sum_{i>j=1}^{N}(u_i^{(k)}\cdot u_j^{(k)})$

TABLE I. Different parts of the formula giving the variance σ^2 of the distribution of the level energies belonging to a given configuration. $a = N(N-1)(4l-N+1)(4l-N+2)$; $b = N(4l-N+2)N'(4l'-N'+2)$

(a) Configuration nl^N: $\sigma^2 = \sum_{i=1}^{4} D_i$, where

$$D_1 = \sum_{k\neq 0}\sum_{k'\neq 0}\left(\frac{2\delta(k,k')}{(2k+1)} - \frac{1}{(2l+1)(4l+1)} - (-1)^{k+k'}\begin{Bmatrix} l & l & k \\ l & l & k' \end{Bmatrix}\right)$$

$$\times \frac{(2l+1)^3}{(4l-1)8l(4l+1)}\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l & k' & l \\ 0 & 0 & 0 \end{pmatrix}^2 aF^k(ll)F^{k'}(ll)$$

$$D_2 = \sum_{k\neq 0}\left(-\frac{1}{(2l+1)(4l+1)} + (-1)^k\begin{Bmatrix} l & l & k \\ l & l & 1 \end{Bmatrix}\right)\frac{(l+1)(2l+1)^2}{2(4l-1)(4l+1)}\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 a\alpha F^k(ll)$$

$$D_3 = \left(-\frac{1}{(2l+1)(4l+1)} + \frac{2}{3} - \begin{Bmatrix} l & l & 1 \\ l & l & 1 \end{Bmatrix}\right)\frac{l(l+1)^2(2l+1)}{2(4l-1)(4l+1)} a\,\alpha^2$$

$$D_4 = \frac{l(l+1)}{4(4l+1)}N(4l-N+2)\zeta_{nl}^2$$

(b) Configuration $nl^N n'l'^{N'}$: $\sigma^2 = \sum_{i=1}^{7} D_i + \sum_{i=1}^{4} D_i'$ (see text)

$$D_5 = \sum_{k\neq 0}\sum_{k'\neq 0} \frac{\delta(k,k')(2l+1)(2l'+1)}{(2k+1)(4l+1)(4l'+1)}\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 bF^k(ll')F^{k'}(ll')$$

$$D_6 = \sum_{k}\sum_{k'}\left(\frac{\delta(k,k')}{(2k+1)} - \frac{1}{4(2l+1)(2l'+1)}\right)\frac{(2l+1)(2l'+1)}{(4l+1)(4l'+1)}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l & k' & l' \\ 0 & 0 & 0 \end{pmatrix}^2 b\,G^k(ll')G^{k'}(ll')$$

$$D_7 = \sum_{k\neq 0}\sum_{k'} (-1)^{k+k'+1}\begin{Bmatrix} l' & l' & k' \\ l & l & k \end{Bmatrix}\frac{(2l+1)(2l'+1)}{(4l+1)(4l'+1)}\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l & k' & l' \\ 0 & 0 & 0 \end{pmatrix}^2 bF^k(ll')G^{k'}(ll')$$

($u^{(k)}$ unitary operator; k odd), where F^k, sometimes called a "forbidden" Slater integral, plays the role of a radial parameter to be fitted in intermediate-coupling studies. The use of F^1 is equivalent to that of α. In conclusion, the formula for D_1 in the first line of Table I applies to all k and k' values (even or odd), provided that, for each k having an odd value, the formula is divided by

$$(2l+1)^2\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 .$$

B. $nl^N n'l'^{N'}$ and more complex configurations

In a configuration with two open shells, all the states can be considered as antisymmetrized products of states of the two subconfigurations nl^N and $n'l'^{N'}$. In this way it is easy to show that the formulas in Table I(a) remain valid for all the products of parameters relevant to only one of the two subconfigurations. The results gathered in Table I(b) concern only the squares and crossed products of $F^k(nl,n'l')$ and $G^k(nl,n'l')$ integrals. The method used for their derivation is exactly analogous to that used in the preceding paragraph.

For obtaining the expression of σ^2 in $nl^N n'l'^{N'}$, one must add to Eq. (3) the analogous expression $\sum_{i=1}^{4} D_i'$, where every radial parameter now corresponds to electrons $n'l'$ and N is changed to N', and $D_5 + D_6 + D_7$ as listed in Table I(b). The latter contributions depend on N and N' like

$$N(4l-N+2)N'(4l'-N'+2) .$$

No crossed product $F^k\zeta$ or $G^k\zeta$ appears in Table I(b), as explained by the argument of the preceding paragraph. For the absence of the crossed product $\zeta_{nl}\zeta_{n'l'}$, a similar argument can be found, in the coupling scheme

$$[nl^N\alpha SLJ, n'l'^{N'}\alpha'S'L'J']J'' .$$

Concerning the crossed products

$$F^k(nl,nl)F^{k'}(n'l',n'l')\,,$$
$$F^k(nl,nl)F^{k'}(nl,n'l')\,,$$
$$F^k(nl,nl)G^{k'}(nl,n'l')\,,$$

and the last two with nl and $n'l'$ exchanged, the coupling scheme

$$(nl^N\alpha SL,n'l'^{N'}\alpha'S'L')S''L''J''$$

can be used. Considering

$$F^k(nl,nl)G^{k'}(nl,n'l')$$

as a typical example, we group, in the first sum of Eq. (2), all the matrix elements corresponding to a given αSL. In this group, the part in $F^k(nl,nl)$ is a common factor, and the other part sums up to a result proportional to $(2S+1)(2L+1)$, which appears in turn as the appropriate weight when the sum is now extended to all αSL terms. After the division by g has been carried out, the first term of Eq. (2) is twice the product of two average quantities and is exactly cancelled by the second term. For the absence of terms in

$$F^k(nl,n'l')F^{k'}(nl,n'l')\quad (k\neq k')\,,$$

which is a result of our calculations, we have no transparent explanation.

Similar arguments apply to the cases of

$$nl^Nn'l'^{N'}n''l''^{N''}$$

and more complex configurations: Table I is sufficient for building the complete expression of σ^2 in all cases, by adding the contributions coming from all relevant subshells and pairs of subshells.

C. Discussion. The σ^2 check

In a previous paper,[12] we have computed numerically the standard deviation of the distribution of energy states in the configurations $3d^4$, $3d^34p$, and $3d^34s$ of Fe V, and compared the results with the values obtained from a direct numerical calculation using the level energies classified by Ekberg[17] with the weight $2J+1$ for each level. Comparisons of this type are satisfactory inasmuch as the different radial parameters are known with accuracy, i.e., inasmuch as the intermediate-coupling interpretation is accurate.

An interesting by-product of this study is the possibility which the formula for σ^2 gives to check the matrices of the coefficients of energy parameters "in the computer." Indeed the methods proposed by Racah,[18] Roth,[19] and others do not apply to all cases. For what may be called the "σ^2 check," proceed as follows: give any value to the radial parameters whose matrix you want to check, then diagonalize all the J matrices, and eventually check that the variance of the eigenvalue distribution agrees with the numerical value obtained with the formula for σ^2 (Table I).

To obtain a more refined description of the distribution of the level energies in a configuration, it would be necessary to compute its third moment, which defines the asymmetry. However this is outside the scope of the present work.

III. STATISTICAL WIDTH OF A TRANSITION ARRAY

The standard deviation of the weighted line wavenumber distribution is the square root of the variance

$$\sigma^2=\mu_2-(\mu_1)^2\,,$$

where

$$\mu_n=\sum_{a,b}\frac{[\langle a|H|a\rangle-\langle b|H|b\rangle]^n w_{ab}}{W} \tag{4}$$

is the nth moment of the distribution. The weight of a transition is its strength w_{ab} and $W=\sum_{a,b}w_{ab}$ is the sum of the weights. The sums $\sum_{a,b}$ run over all eigenstates a and b of respective configurations A and B *in intermediate coupling*. In the following, w_{ab} can be replaced by $|\langle a|Z|b\rangle|^2$, where $Z=\sum_i z_i$ is, within a constant factor, the z component of the usual dipole operator.

The question of intermediate coupling may be dealt with first. Considering, as an example, the quantity

$$q=\sum_{a,b}\langle a|H|a\rangle\langle b|H|b\rangle\langle a|Z|b\rangle\langle b|Z|a\rangle \tag{5}$$

occuring in μ_2, we can write it equivalently

$$q=\sum_{a,b,m,n}\langle a|Z|b\rangle\langle b|H|m\rangle\langle m|Z|n\rangle\langle n|H|a\rangle\,, \tag{6}$$

where indices a and n (b and m) run over all the eigenstates of configuration A (B). The second-quantization method, which was introduced by Judd[20] in atomic spectroscopy, makes it possible to write the operators in the form

$$F=\sum_{\alpha,\beta}a_\alpha^\dagger\langle\alpha|f|\beta\rangle a_\beta \tag{7}$$

for monoelectronic operators Z and Λ, and

$$G=\frac{1}{2}\sum_{\gamma,\delta,\epsilon,\varphi}a_\gamma^\dagger a_\delta^\dagger\langle\gamma_1\delta_2|g_{12}|\epsilon_1\varphi_2\rangle a_\varphi a_\epsilon \tag{8}$$

for the electrostatic interaction. This enables the specialization of the different operators, occuring in sums like q, to the relevant electronic orbitals. Suppose that we are interested in the transitions between $A=nl^{N+1}$ and $B=nl^Nn'l'$ and in the G term of H. Then the operator Z occuring in the first matrix element of Eq. (6) can be replaced by expression (7) with α (β) running over all states

nlm_lm_s ($n'l'm_l'm_s'$) of one nl ($n'l'$) electron. In the same way, in the second matrix element of Eq. (6), G can be replaced by expression (8) where the pairs (γ, δ) and (ϵ, φ) are either both pairs of nl-electron states or both pairs of one nl- and one $n'l'$-electron state.

After such replacements have been made in Eq. (6), each one of the indices a, b, m, and n can be allowed to run over a complete set of states, with the consequence that the sums over b, m, and n can be dropped together with the corresponding kets and bras. We are left with

$$q = \sum_a \langle a | \mathrm{Op} | a \rangle , \tag{9}$$

where the Hermitian operator Op is a sum over magnetic quantum numbers m_l and m_s of products of many annihilation and creation operators and of mono- and bi-electronic matrix elements of Z, Λ, and G, and where states a can evidently be replaced by states a' in any other coupling. In the following, we sometimes use the fact that only the scalar part of Op is of interest: this property stems from the fact that the sum

$$\sum_M (\alpha JM | T_0^{(k)} | \alpha JM)$$

for a tensor $T^{(k)}$ with $k \neq 0$ is zero.

The direct calculation of a quantity like q for arbitrary N would be very cumbersome. It is quicker, in the first step, to try to determine the dependence of each part of σ^2 (or of μ_1 or μ_2) on N and, in the second step, to compute directly its formal expression for one or two simple cases (nl shell almost empty or almost closed). As an example, we present in the Appendix the application of this general procedure to the most complicated case, which concerns the $F^k(nl, nl)$ integrals for the $nl^{N+1} - nl^N n'l'$ transitions.

A. nl^{N+1}-$nl^N\ n'l'$ transitions

In the case of the transitions between configurations $A = nl^{N+1}$ and $B = nl^N n'l'$, the variance σ^2 is a linear combination of (i) squares and cross products of "internal" Slater integrals $F^k(nl, nl)$ (which we denote F_A^k and F_B^k in configurations A and B, respectively) and of "external" Slater integrals $F^k(nl, n'l')$ and $G^k(nl, n'l')$; (ii) squares and cross products of spin-orbit integrals ζ_{nl} (which we denote $\zeta_{nl,A}$ and $\zeta_{nl,B}$ in respective configurations A and B) and $\zeta_{n'l'}$.

No cross products of Slater and spin-orbit integrals occur. Indeed a quantity like

$$q' = \sum_{a,b} (a | Z | b)(a | G | a)(b | \Lambda | b)(b | Z | a) \tag{10}$$

corresponds to an operator Op [see Eq. (9)] of rank 1 in the spin space, whose scalar part is therefore also of rank 1 in the orbital space. To such an operator the Landé center-of-gravity rule applies, and yields $q' = 0$.

The complete results for this kind of transitions are presented in Table II. σ^2 is equal to the sum $\sum_{i=1}^{7} H_i$. In the H_i quantities, the factors depending on N are labeled x, y, z, u, v, and w and are defined in the caption of the table. With the assumption $F_A^k = F_B^k$, the N dependence of H_1 would become

$$x + y - 2z \equiv 2N(4l-1)(4l-N+1) ,$$

a result in accordance with Eq. (3.6) of Moszkowski.[10] The resemblance between expressions H_1 and D_1 (Table I) is considered at the end of the next paragraph.

B. $nl^N\ n'l'$ - $nl^N\ n''l''$ transitions

The complete expression for σ^2 in the case of the transitions between configurations $nl^N n'l'$ and $nl^N n''l''$ is presented in Table III. In the expression

$$\sigma^2 = \sum_{i=1}^{8} E_i + \sum_{i=2}^{4} E_i' + E_7'$$

not only the crossed products of Slater and spin-orbit integrals are missing (see above), but also those of the $F^k(l,l)F^{k'}(l,l')$ and $F^k(l,l)G^{k'}(l,l')$ types.

The resemblance between expressions E_1, E_2, E_3, E_4 (Table III) and D_1, D_5, D_6, D_7 (Table I) is noteworthy. It can be explained through the following argument. Consider the sum

$$\sum_{a,b} (a | G | a)(a | G | a)(a | Z | b)(b | Z | a) \tag{11}$$

$$(a \in nl^N n'l' ,\ b \in nl^N n''l'')$$

which leads to expressions E_1–E_4. Replace Z by its second-quantization expression [Eq. (7)] and carry out the sum over b: because it is acting between $(a|$ and $|a)$, the operator $\sum_b Z | b)(b | Z$ can be written

$$\begin{aligned}
&\sum_{\alpha\beta\gamma\delta} a_\alpha^\dagger (\alpha | z | \beta) a_\beta a_\gamma^\dagger (\gamma | z | \delta) a_\delta \\
&\quad = \sum_{\alpha\beta\delta} a_\alpha^\dagger (\alpha | z | \beta)(\beta | z | \delta) a_\delta \\
&\quad = \sum_\alpha a_\alpha^\dagger \tfrac{1}{3} | (n'l' || r || n''l'') |^2 a_\alpha \\
&\quad = \tfrac{1}{3} | (n'l' || r || n''l'') |^2
\end{aligned}$$

where α, δ (β, γ) run over all the states of an $n'l'$ $(n''l'')$ electron. Therefore the strength $(a | Z | b)$ $(b | Z | a)$ of transition a-b plays no role in the considered expression, and the remaining computation is identical with that of the width of the state-energy distribution of configuration $nl^N n'l'$ (Sec.

TABLE II. Different parts of the formula giving the variance σ^2 of the energy distribution of the transitions between nl^{N+1} and $nl^Nn'l'$ configurations. F^k_A and F^k_B are the Slater integrals $F^k(nl,nl)$ in the configurations $A=nl^{N+1}$ and $B=nl^Nn'l'$ respectively. $\zeta_{nl,A}$ and $\zeta_{nl,B}$ are the spin-orbit integrals in the respective configurations.

$x=N(N+1)(4l-N)(4l-N+1)$, $u=N(4l-N)(4l-N+1)$,

$y=N(N-1)(4l-N+1)(4l-N+2)$, $v=N(N-1)(4l-N+1)$,

$z=N(N-1)(4l-N)(4l-N+1)$, $w=N(4l-N+1)$.

$$H_1=\sum_{k\neq 0}\sum_{k'\neq 0}\left(\frac{2\delta(k,k')}{(2k+1)}-\frac{1}{(2l+1)(4l+1)}-(-1)^{k+k'}\begin{Bmatrix} l & l & k \\ l & l & k' \end{Bmatrix}\right)\frac{(2l+1)^3}{(4l-1)8l(4l+1)}$$

$$\times\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l & k' & l \\ 0 & 0 & 0 \end{pmatrix}^2(xF^k_A F^{k'}_A+yF^k_B F^{k'}_B-2zF^k_A F^{k'}_B)$$

$$H_2=\sum_{k\neq 0}\sum_{k'\neq 0}\left(\frac{2(-1)^k}{(2k+1)}\delta(k,k')\begin{Bmatrix} l' & l' & k \\ l & l & 1 \end{Bmatrix}-(-1)^k\begin{Bmatrix} l & l & k' \\ l & l & k \end{Bmatrix}\begin{Bmatrix} l & l & k' \\ l' & l' & 1 \end{Bmatrix}-\frac{1}{(2l+1)(4l+1)}\begin{Bmatrix} l & l & k' \\ l' & l' & 1 \end{Bmatrix}\right)$$

$$\times\frac{(2l+1)^3(2l'+1)}{(4l-1)2l(4l+1)}\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l' & k' & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l & k' & l \\ 0 & 0 & 0 \end{pmatrix}[uF^k_A F^{k'}(ll')+vF^k_B F^{k'}(ll')]$$

$$H_3=\sum_{k\neq 0}\sum_{k'}\left[-2\begin{Bmatrix} k & k' & 1 \\ l' & l & l \end{Bmatrix}^2+\begin{Bmatrix} l' & l' & k \\ l & l & 1 \end{Bmatrix}\begin{Bmatrix} l' & l' & k \\ l & l & k' \end{Bmatrix}-\frac{1}{(2l+1)(4l+1)}\left(\frac{2}{3}\delta(k',1)-\frac{1}{(2l'+1)}\right)\right]$$

$$\times\frac{(2l+1)^3(2l'+1)}{(4l-1)2l(4l+1)}\begin{pmatrix} l & k' & l' \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2[uF^k_A G^{k'}(ll')+vF^k_B G^{k'}(ll')]$$

$$H_4=\sum_{k\neq 0}\sum_{k'\neq 0}\left(\frac{2\delta(k,k')}{(2l'+1)(2k+1)}-\begin{Bmatrix} l & l & k \\ l & 1 & l' \\ k' & l' & l' \end{Bmatrix}-\frac{1}{(4l+1)}\begin{Bmatrix} l & l' & 1 \\ l' & l & k \end{Bmatrix}\begin{Bmatrix} l & l' & 1 \\ l' & l & k' \end{Bmatrix}\right)\frac{(2l+1)^2(2l'+1)^2}{4l(4l+1)}$$

$$\times\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l & k' & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k' & l' \\ 0 & 0 & 0 \end{pmatrix}wF^k(ll')F^{k'}(ll')$$

$$H_5=\sum_{k}\sum_{k'}\left[\frac{2\delta(k,k')}{(2l'+1)(2k+1)}-\begin{Bmatrix} l & l' & k \\ l' & 1 & l \\ k' & l & l' \end{Bmatrix}-\frac{1}{(4l+1)}\left(\frac{2}{3}\delta(k,1)-\frac{1}{(2l'+1)}\right)\left(\frac{2}{3}\delta(k',1)-\frac{1}{(2l'+1)}\right)\right]$$

$$\times\frac{(2l+1)^2(2l'+1)^2}{4l(4l+1)}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l & k' & l' \\ 0 & 0 & 0 \end{pmatrix}^2 wG^k(ll')G^{k'}(ll')$$

$$H_6=\sum_{k\neq 0}\sum_{k'}\left[\frac{(-1)^k}{(2l'+1)}\begin{Bmatrix} l' & l' & k \\ l & l & k' \end{Bmatrix}-2(-1)^k\begin{Bmatrix} k & k' & 1 \\ l & l' & l' \end{Bmatrix}\begin{Bmatrix} k & k' & 1 \\ l' & l & l \end{Bmatrix}-\frac{1}{(4l+1)}\begin{Bmatrix} l & l' & 1 \\ l' & l & k \end{Bmatrix}\left(\frac{2}{3}\delta(k',1)-\frac{1}{(2l'+1)}\right)\right]$$

$$\times\frac{(2l+1)^2(2l'+1)^2}{2l(4l+1)}\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l & k' & l' \\ 0 & 0 & 0 \end{pmatrix}^2 wF^k(ll')G^{k'}(ll')$$

For the spin-orbit contribution:

$$H_7=(N+1)(4l-N+1)\frac{l(l+1)}{4(4l+1)}\zeta^2_{nl,A}+N(4l-N+2)\frac{l(l+1)}{4(4l+1)}\zeta^2_{nl,B}+\frac{l'(l'+1)}{4}\zeta^2_{n'l'}$$

$$-N(4l-N+1)\frac{l(l+1)}{2(4l+1)}\zeta_{nl,A}\zeta_{nl,B}-(4l-N+1)\frac{l(l+1)+l'(l'+1)-2}{4(4l+1)}\zeta_{nl,A}\zeta_{n'l'}-N\frac{l(l+1)+l'(l'+1)-2}{4(4l+1)}\zeta_{nl,B}\zeta_{n'l'}$$

TABLE III. Different parts of the formula giving the variance σ^2 of the energy distribution of the transitions between $nl^N n'l'$ and $nl^N n''l''$ configurations.

$$\Delta F^k = F^k(ll)(\text{in } l^N l') - F^k(ll)(\text{in } l^N l'') , \quad \Delta\zeta_{nl} = \zeta_{nl}(\text{in } l^N l') - \zeta_{nl}(\text{in } l^N l'') ,$$

$$y = N(N-1)(4l-N+1)(4l-N+2), \quad t = N(4l-N+2) .$$

$$E_1 = \sum_{k\neq 0}\sum_{k'\neq 0}\left(\frac{2\delta(k,k')}{(2k+1)} - \frac{1}{(2l+1)(4l+1)} - (-1)^{k+k'}\begin{Bmatrix} l & l & k \\ l & l & k' \end{Bmatrix}\right)$$

$$\times\frac{(2l+1)^3}{(4l-1)8l(4l+1)}\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l & k' & l \\ 0 & 0 & 0 \end{pmatrix}^2 y\Delta F^k \Delta F^{k'}$$

$$E_2 = \sum_{k\neq 0}\sum_{k'\neq 0}\frac{\delta(k,k')}{(2k+1)}\,\frac{(2l+1)(2l'+1)}{(4l+1)}\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 tF^k(ll')F^{k'}(ll')$$

E_2': same as E_2 with l'' replacing l'

$$E_3 = \sum_{k}\sum_{k'}\left(\frac{\delta(k,k')}{(2k+1)} - \frac{1}{4(2l+1)(2l'+1)}\right)\frac{(2l+1)(2l'+1)}{(4l+1)}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l & k' & l' \\ 0 & 0 & 0 \end{pmatrix}^2 tG^k(ll')G^{k'}(ll')$$

E_3': same as E_3 with l'' replacing l'

$$E_4 = \sum_{k\neq 0}\sum_{k'}(-1)^{k+k'+1}\begin{Bmatrix} l' & l' & k \\ l & l & k' \end{Bmatrix}\frac{(2l+1)(2l'+1)}{(4l+1)}\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l & k' & l' \\ 0 & 0 & 0 \end{pmatrix}^2 tF^k(ll')G^{k'}(ll')$$

E_4': same as E_4 with l'' replacing l'

$$E_5 = \sum_{k\neq 0}\sum_{k'\neq 0}\frac{2(-1)^k\delta(k,k')}{(2k+1)}\begin{Bmatrix} l'' & l'' & k \\ l' & l' & 1 \end{Bmatrix}\frac{(2l+1)(2l'+1)(2l''+1)}{(4l+1)}$$

$$\times\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l'' & k & l'' \\ 0 & 0 & 0 \end{pmatrix} tF^k(ll')F^{k'}(ll'')$$

$$E_6 = \sum_{k}\sum_{k'}\left(-2\begin{Bmatrix} k & k' & 1 \\ l'' & l' & l \end{Bmatrix}^2 + \frac{1}{2(2l+1)(2l'+1)(2l''+1)}\right)\frac{(2l+1)(2l'+1)(2l''+1)}{(4l+1)}$$

$$\times\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l & k' & l'' \\ 0 & 0 & 0 \end{pmatrix}^2 tG^k(ll')G^{k'}(ll'')$$

$$E_7 = \sum_{k\neq 0}\sum_{k'}(-1)^{k'+1}\begin{Bmatrix} l'' & l'' & k \\ l' & l' & 1 \end{Bmatrix}\begin{Bmatrix} l'' & l'' & k \\ l & l & k' \end{Bmatrix}\frac{(2l+1)(2l'+1)(2l''+1)}{(4l+1)}$$

$$\times\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l & k' & l'' \\ 0 & 0 & 0 \end{pmatrix}^2 tF^k(ll')G^{k'}(ll'')$$

E_7': same as E_7 with l' and l'' interchanged

For the spin-orbit contribution:

$$E_8 = \frac{l(l+1)}{4(4l+1)}t(\Delta\zeta_{nl})^2 + \frac{l'(l'+1)}{4}\zeta^2_{n'l'} + \frac{l''(l''+1)}{4}\zeta^2_{n''l''} - \frac{l'(l'+1)+l''(l''+1)-2}{4}\zeta_{n'l'}\zeta_{n''l''}$$

II). This argument can also be used for explaining the analogy between expressions H_1 (Table II) and D_1 (Table I).

Moreover, it can be easily understood why the differences

$$\Delta F^k = F^k(\text{in } l^N l') - F^k(\text{in } l^N l'')$$

of the "internal" Slater integrals appear in E_1 (Table III). If the other parameters were zero, both configurations would be split by the energy contributions in $F^k(l,l)$ only. Due to the intensity selection rules, the transitions would occur only between states with the same l^N part, and would coalesce into just one line if the ΔF^k quantities were zero.

IV. AVERAGE WAVE NUMBER OF A TRANSITION ARRAY

We turn now to the results for the weighted average energy T_{av} of the transition array between two configurations. More precisely, our interest lies in determining the relationship of T_{av} with the difference of the average energies E_{av} of the states of the two involved configurations. For these average energies, tables are available.[21]

The weighted average wave number of a transition array (the weight being the transition strength) is its moment μ_1 [Eq. (4)]. It is present in the expression for σ^2 (Sec. III) and has been computed along the same principles as μ_2. Using an argument analogous to that developed about the computation of the expression (11), it is shown immediately that

$$T_{\text{av}}(l^N l'' \to l^N l') = E_{\text{av}}(l^N l'') - E_{\text{av}}(l^N l') . \tag{12}$$

But the same type of quick argument does not hold for computing the quantity

$$\sum_{a,b} (b|G|b)(b|Z|a)(a|Z|b) ,$$

with $a \in A = l^{N+1}$ and $b \in B = l^N l'$, which is part of $T_{\text{av}}(l^N l' \to l^{N+1})$. As a result of the formal computation, we obtained for the difference

$$\delta E(l^N l' \to l^{N+1}) = T_{\text{av}}(l^N l' \to l^{N+1}) - [E_{\text{av}}(l^N l') - E_{\text{av}}(l^{N+1})] \tag{13}$$

the formula

$$\delta E = N \frac{(2l+1)(2l'+1)}{4l+1} \left(\sum_{k \neq 0} f_k F^k(l\,l') + \sum_k g_k G^k(l\,l') \right), \tag{14}$$

with

$$f_k = \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & k & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l & k & l \\ l' & 1 & l' \end{Bmatrix}$$

$$g_k = \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \left(\frac{2}{3}\delta(k,1) - \frac{1}{2(2l+1)(2l'+1)} \right).$$

Thus there exists a shift between the weighted average energy of a transition array and the difference of average energies of configurations of these types; its formal expression is not symmetrical with respect to the half-filled l-shell. This shift has already been put into evidence by Cowan[8] in 1968, for the $3p^{N+1}$-$3p^N 3d$ transitions in the series Fe IX – Fe XIII. Other examples are presented in the following paragraphs.

V. COMPLEMENTARY CONFIGURATIONS

From the results for the l^{N+1}-$l^N l'$ and $l^N l'$-$l^N l''$ types of transitions, those for the respective complementary types

$$l^{4l-N+1} l'^{4l'+2} - l^{4l-N+2} l'^{4l'+1}$$

and

$$l^{4l-N+2} l'^{4l'+1} l''^{4l''+2} - l^{4l-N+2} l'^{4l'+2} l''^{4l''+1}$$

can be immediately deduced.

It is well known that, formally, the relative energies of the levels are identical in complementary configurations,[15] but for the change of sign of the coefficients of the spin-orbit parameters, and that the same property is valid for the matrix elements of nonscalar tensor operators,[22] except for a possible phase factor. Therefore quantities like those in expression (11) are transposable to complementary configurations. The same is true for the δE shift [Eq. (14)], as can be shown by considering the effect of adding a constant to either one of the G matrix elements in the definition of T_{av}

$$T_{\text{av}} = \frac{\sum_{a,b} |\langle a|Z|b\rangle|^2 [\langle b|G|b\rangle - \langle a|G|a\rangle]}{\sum_{a,b} |\langle a|Z|b\rangle|^2} . \tag{15}$$

In conclusion, for both the variance σ^2 (Sec. III) and the shift δE (Sec. IV), the formulas for complementary types of configurations are identical, e.g.,

$$\delta E(l^N l' \to l^{N+1}) \equiv \delta E(l^{4l-N+2} l'^{4l'+1} \to l^{4l-N+1} l'^{4l'+2}) .$$

This correspondence, together with the evident relations

$$\sigma^2(C \to C') = \sigma^2(C' \to C)$$

and

$$\delta E(C \to C') = -\delta E(C' \to C)$$

valid for any pair of configurations C, C', allows one to treat the case of some types of transitions involving holes rather than electrons; for instance, the cases $1s2p^6 nl^N \to 1s^2 2p^5 nl^N$ and $nl^{4l+2-N}1s \to nl^{4l+2-N}2p$ are identical (in particular, $\delta E = 0$).

VI. NUMERICAL APPLICATIONS

A. Numerical tables

In Tables IV and V, we list the numerical values of the N-independent parts of the angular coefficients in σ^2 of the electrostatic-parameter products appearing in Tables II and III, respectively.

Table IV, for the l^{N+1}-$l^N l'$ transitions, includes all the cases for which $l, l' \leqslant 3$, except s^2-sp. Table V, for the $l^N l'$-$l^N l''$ transitions, includes all the cases for which $l=1$ or 2 and $l', l'' \leqslant 3$. It must be noted that all the entries in these tables have been multiplied by 10^4, and that using once *all* the numbers of the relevant column insures that the correct total expression for the electrostatic part of σ^2 is computed.

B. Example: the Fe V spectrum

For an explicit check of our results, we chose the spectrum of Fe V, where Ekberg[17] classified 622 and 360 lines in the $3d^4$-$3d^3 4p$ and $3d^3 4s$-$3d^3 4p$ arrays, respectively.

Starting from the matrices for the angular coefficients of the energy parameters and of the transition amplitudes, we checked that the explicit computation of all the transition energies and strengths yielded exactly the same value of σ^2 as that obtained with Tables IV and V. Moreover, using Ekberg's values for the radial parameters, we could compare our calculated σ^2 value to that deduced from Ekberg's experimental data for the line wave numbers and estimated intensities. That comparison, published previously,[12] showed a reasonable agreement. It was noted that the width of each transition array is smaller than that of either of the two relevant configurations (up to four times smaller in the case of the $3d^3 4s$-$3d^3 4p$ array). Following an argument given by Cowan[8] in 1973, it can be predicted that the $l^N l'$-$l^N l''$ arrays are particularly narrow. The dominant radial integrals are generally the core electrostatic integrals $F^k(nl, nl)$. But they appear in σ^2 (line E_1 in Table III) only through the differences

$$\Delta F^k = F^k(\text{in } l^N l') - F^k(\text{in } l^N l''),$$

which are much smaller.

VII. APPLICATION TO THE SPECTRUM OF MOLYBDENUM

A. Comparison between the experimental and theoretical spectra

The spectrum of molybdenum is of great importance for tokamak research. Furthermore, it has been recorded recently between 10 and 100 Å not only in tokamaks[1] but also in high-power vacuum sparks[2] and in laser-produced plasmas.[3] We have applied the above formulas to the following transitions: $3d^{N+1} - 3d^N 4p$, $3d^{N+1} - 3d^N 4f$, $3d^{N+1} - 3d^N 5p$, and $3d^{N+1} - 3d^N 5f$. The energies and Slater integrals have been computed by the relativistic-parametric-potential method, using the RELAC code.[23-25] In order to use our nonrelativistic formulas, the relativistic Slater integrals were averaged following the prescription of Larkins.[26]

In Figs. 1 and 2, we compare transition patterns explicitly computed in Mo XVI $3d^9 - 3d^8 4p$ and $3d^9 - 3d^8 4f$ with a Gaussian curve whose mean value and variance are calculated using formulas obtained above. The computed lines are displayed with an intensity proportional to their strength and with a linewidth assumed to be equal to 0.03 Å, which enables the summation effect of neighboring lines to be apparent. These two cases are very different. In the $3d - 4p$ case (Fig. 1) the Gaussian curve nearly fits the envelope of the group of lines whereas it is not so in the $3d - 4f$ case (Fig. 2). However, both cases are interesting because they clearly show that the probability of finding a line belonging to one pattern at a large distance from the average is very small although not zero. This is all the more striking since the ground configuration in these two cases has only two levels, which is really a limit for the usefulness of a statistical description.

Figure 3 shows a theoretical spectrum consisting of a superposition of several individual transition arrays computed separately. It is compared to the experimental spectrum of molybdenum (shifted upwards for sake of clarity) obtained from a higher-power vacuum spark.[2] The relative weights of the different ionization stages are fitted to experiment in a simple manner: they vary linearly between 1 for Mo XVI and 0.1 for Mo XXIII. The relative intensities of the different transition arrays within each ionization stage were taken as equal to the theoretical ratio obtained for Mo XV[27] in a plasma having the characteristics: $n_e = 10^{18}$ cm^{-3}, $kT_e = 200$ eV. It may be noted that the transition arrays, here, are not described by Gaussian curves but actually by Lorentzian profiles, possessing a full width at half maximum equal to that of a Gaussian whose variance is computed with the formulas of the preceding paragraphs. This was done in order to reproduce the effect of the photographic plate, having an apparent strong background.

It can be seen that between 36 and 50 Å, where one does not expect any other type of transition, the model agrees very well with experiment. Between 20 and 36 Å, the agreement is still good, but one sees that there are some experimental peaks which have the same wavelengths as some "dips" in the theoretical spectrum. This suggests

TABLE IV. N-independent parts of the coefficients of the parameter products in the variance σ^2 for $l^{N+1}-l^Nl'$ transitions. (All entries have to be multiplied by 10^{-4}.) F^k_A and F^k_B are the Slater integrals $F^k(ll)$ in the configurations $A=l^{N+1}$ and $B=l^Nl'$ respectively.

$$x=N(N+1)(4l-N)(4l-N+1)\ ,\qquad u=N(4l-N)(4l-N+1)\ ,$$

$$y=N(N-1)(4l-N+1)(4l-N+2)\ ,\quad v=N(N-1)(4l-N+1)\ ,$$

$$z=N(N-1)(4l-N)(4l-N+1)\ ,\qquad w=N(4l-N+1)\ .$$

	k	k'	$p^{N+1}-p^Ns$ (10^{-4})	$p^{N+1}-p^Nd$ (10^{-4})	$d^{N+1}-d^Np$ (10^{-4})	$d^{N+1}-d^Nf$ (10^{-4})	$f^{N+1}-f^Nd$ (10^{-4})
$xF^k_AF^{k'}_A+yF^k_BF^{k'}_B-2zF^k_AF^{k'}_B$	2	2	12	12	1.7033	1.7033	0.4986
	2	4			−0.3214	−0.3214	0.0598
	2	6					−0.0894
	4	2			−0.3214	−0.3214	0.0598
	4	4			0.8034	0.8034	0.0952
	4	6					−0.0151
	6	2					−0.0894
	6	4					−0.0151
	6	6					0.1582
$uF^k_AF^{k'}(ll')+vF^k_BF^{k'}(ll')$	2	2		−24	−4.7691	−5.4504	−1.7095
	2	4				0.4285	−0.1252
	4	2			0.8998	1.0284	−0.2049
	4	4				−1.0712	−0.1995
	6	2					0.3065
	6	4					0.0317
$uF^k_AG^{k'}(ll')+vF^k_BG^{k'}(ll')$	2	1	−80	−8	−3.4853	0.7044	−0.5478
	2	3		−30.8571	0.7481	−3.4005	−0.3862
	2	5				0.9738	0.3415
	4	1			−0.8398	−1.1312	−0.0062
	4	3			−3.6250	0.5827	−0.3512
	4	5				−2.4346	0.0415
	6	1					−0.2926
	6	3					0.0557
	6	5					−0.6851
$wF^k(ll')F^{k'}(ll')$	2	2		70.2857	32.7160	20.0554	13.2781
	2	4				0.4199	0.2415
	4	2				0.4199	0.2415
	4	4				7.8576	5.1265
$wG^k(ll')G^{k'}(ll')$	1	1	266.6667	77.3333	88.2030	49.0804	52.5540
	1	3		15.4286	2.0282	−2.4859	−1.4384
	1	5				4.3901	1.6955
	3	1		15.4286	2.0282	−2.4859	−1.4384
	3	3		39.0437	18.5941	10.8956	6.7971
	3	5				−1.0180	−0.5747
	5	1				4.3901	1.6955
	5	3				−1.0180	−0.5747
	5	5				7.5390	4.8893
$wF^k(ll')G^{k'}(ll')$	2	1		−16	−25.5144	−3.4266	−8.5658
	2	3		4.4082	−1.2850	13.8742	7.4459
	2	5				−7.2532	−4.3831
	4	1				−6.7187	−6.0111
	4	3				−3.9193	−2.7312
	4	5				1.5328	0.6684

TABLE V. N-independent parts of the coefficients of the parameter products in the variance σ^2 for $l^N l' - l^N l''$ transitions. (All entries have to be multiplied by 10^{-4}.)

$\Delta F^k = F^k(ll)$ (in $l^N l'$) $- F^k(ll)$ (in $l^N l''$) ,

$y \quad = N(N-1)(4l-N+1)(4l-N+2)$,

$t \quad = N(4l-N+2)$.

	k	k'	$p^N s - p^N p'$ (10^{-4})	$p^N d - p^N p'$ (10^{-4})	$p^N d - p^N f$ (10^{-4})	$d^N p - d^N s$ (10^{-4})	$d^N p - d^N d'$ (10^{-4})	$d^N f - d^N d'$ (10^{-4})
$y\Delta F^k \Delta F^{k'}$	2	2	12	12	12	1.7033	1.7033	1.7033
	2	4				−0.3214	−0.3214	−0.3214
	4	2				−0.3214	−0.3214	−0.3214
	4	4				0.8034	0.8034	0.8034
$tF^k(ll')F^{k'}(ll')$	2	2		45.7143	45.7143	25.3968	25.3968	16.9312
	4	4						6.4133
$tG^k(ll')G^{k'}(ll')$	1	1	166.6667	168.8889	168.8889	93.8272	93.8272	93.1973
	1	3		−5.7143	−5.7143	−3.1746	−3.1746	−0.9070
	1	5						−1.0307
	3	1		−5.7143	−5.7143	−3.1746	−3.1746	−0.9070
	3	3		27.8134	27.8134	15.4519	15.4519	7.6594
	3	5						−0.4581
	5	1						−1.0307
	5	3						−0.4581
	5	5						6.1048
$tF^k(ll')G^{k'}(ll')$	2	1		−53.3333	−53.3333	−29.6296	−29.6296	−21.7687
	2	3		−9.7959	−9.7959	−5.4422	−5.4422	4.4344
	2	5						−4.5810
	4	1						−9.0703
	4	3						−4.0312
	4	5						−0.2082
$tF^k(ll'')F^{k'}(ll'')$	2	2	64	64	42.6667		18.1406	18.1406
	4	4					10.0781	10.0781
$tG^k(ll'')G^{k'}(ll'')$	0	0	1944.4444	1944.4444			1100	1100
	0	2	−22.2222	−22.2222			−3.1746	−3.1746
	0	4					−3.1746	−3.1746
	2	0	−22.2222	−22.2222			−3.1746	−3.1746
	2	2	55.1111	55.1111	58.0408	33.3333	17.2336	17.2336
	2	4			−2.7211		−0.9070	−0.9070
	4	0					−3.1746	−3.1746
	4	2			−2.7211		−0.9070	−0.9070
	4	4			16.7968		9.1711	9.1711
$tF^k(ll'')G^{k'}(ll'')$	2	0	−266.6667	−266.6667			−63.4921	−63.4921
	2	2	−10.6667	−10.6667	−27.4286		3.8873	3.8873
	2	4			−8.4656		−5.1830	−5.1830
	4	0					−63.4921	−63.4921
	4	2					−5.1830	−5.1830
	4	4					−0.1440	−0.1440
$tF^k(ll')F^{k'}(ll'')$	2	2		−64	−73.1429		−25.3968	−29.0249
	4	4						−6.7187
$tG^k(ll')G^{k'}(ll'')$	1	0	−333.3333	−844.4444			−281.4815	−434.9206
	1	2	−133.3333	14.2222	−180.5714	−44.4444	−25.3968	−0.9070
	1	4			8.4656		4.2328	2.7211
	3	0		28.5714			9.5238	4.2328
	3	2		−70.8571	7.0671	−28.5714	1.1662	−15.3763
	3	4			−41.2051		−20.6025	1.0174
	5	0						4.8100
	5	2						1.3743
	5	4						−13.8956

TABLE V. *(Continued)*

	k	k'	p^Ns-p^Np' (10^{-4})	p^Nd-p^Np' (10^{-4})	p^Nd-p^Nf (10^{-4})	d^Np-d^Ns (10^{-4})	d^Np-d^Nd' (10^{-4})	d^Nf-d^Nd' (10^{-4})
$tF^k(ll')G^{k'}(ll'')$	2	0		133.3333			44.4444	50.7936
	2	2		5.3333	23.5102	0	−2.7211	−3.1098
	2	4			7.2562		3.6281	4.1464
	4	0						21.1640
	4	2						1.7277
	4	4						0.0480
$tF^k(ll'')G^{k'}(ll')$	2	1	0	37.3333	42.6667		14.8148	18.6589
	2	3		6.8571	7.8367		2.7211	−3.8009
	2	5						3.9265
	4	1					0	4.7511
	4	3					0	2.1116
	4	5						0.1091

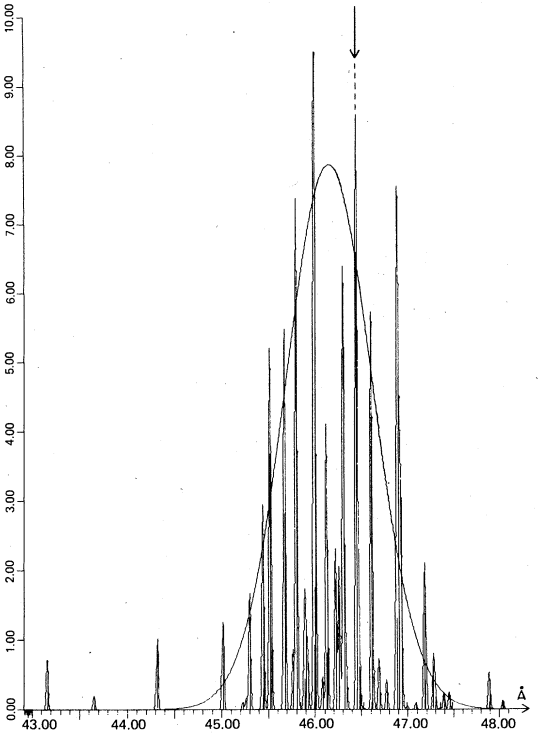

FIG. 1. Transition array Mo XVI $3d^9$-$3d^84p$. Comparison of the computed wavelengths and intensities of individual lines with the theoretical distribution (assumed to be Gaussian), using moments calculated with the formulas presented in the text and tables. The arrow indicates the place where the maximum of the Gaussian curve would be if δE [Eq. (13)] were not taken into account.

that one should consider some additional transition arrays like $3d^{N+1}-3d^N6f$, etc., as well as $3p^63d^N-3p^53d^N4s$, etc., but the relative intensities of these transitions have not yet been calculated.

B. Analysis of the N dependence

Figure 4 shows the shift, in wavelength, corresponding to δE defined by Eq. (13), for transitions $3d^{N+1}-3d^N4p$ and $3d^{N+1}-3d^N4f$. Please note that the values quoted here differ by nearly a factor of 2 from the entries in Table 2 of Ref. 12, which are erroneous. It is clear that this shift is nearly proportional to N and is not symmetrical with respect to the half shell. Its very large value for Mo XVI $3d^9-3d^84f$ is illustrated on Fig. 2 by the arrow which indicates the place of the wavelength corresponding to the difference between centroids of configurations.

In Fig. 5 we have plotted the spectral widths of the transition arrays versus N. Here, the symmetry around the half-filled subshell appears only for $3d-4p$-type transitions and not for the $3d-4f$ type. This can be explained by the behavior of the Slater integrals as a function of N (or stages of ionization). It occurs that the largest numerical contributions to the formula of σ^2 are the first two terms H_1 and H_2 (Table II), which are actually of different signs. The relevant integrals in $3d^N4p$ do not change very much with N, yielding a nicely symmetric curve for σ. On the contrary, the variation with N of the $3d^N4f$ integrals is quite conspicuous, yielding the other curve of Fig. 5. Thus, considering a series of ionization stages of one element, it is difficult to predict which one will give the broadest arrays without evaluating the different Slater integrals explicitly.

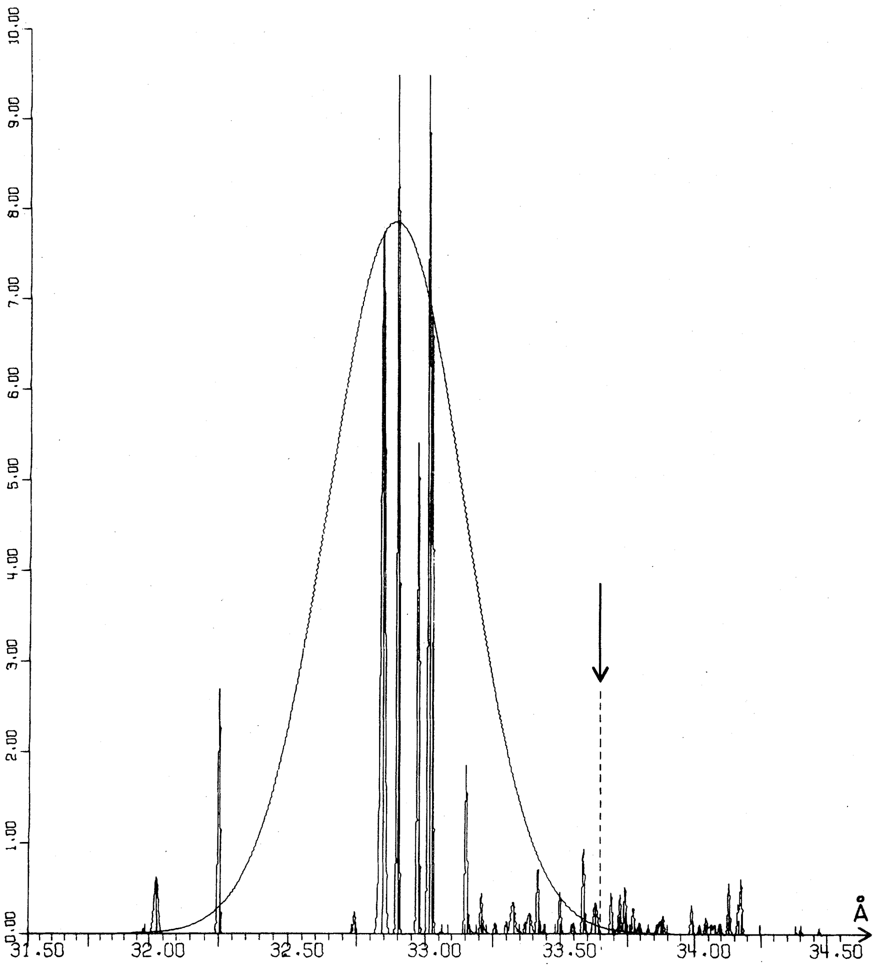

FIG. 2. Transition array Mo XVI $3d^9$-$3d^8 4f$. Comparison of the computed wavelengths and intensities of individual lines with the theoretical distribution (assumed to be Gaussian), using moments calculated with the formulas presented in the text and tables. The arrow indicates the place where the maximum of the Gaussian curve would be if δE [Eq. (13)] were not taken into account.

VIII. DISCUSSION

It is obvious that the results of our formal study can be useful when the transition arrays of interest are composed of numerous lines, and even more so when these lines cannot be observed separately. The case where the number of levels is small in both involved configurations is therefore not relevant.

When comparing these results with experiment, one must be aware of the underlying physical conditions, which may not always be satisfied. The formulas for the width and mean of a transition array suppose that all the *states* of the upper configuration are equally populated, i.e., that the levels are populated according to the statistical weight population (SWP). This happens if the plasma is in local thermodynamic equilibrium (LTE), and if the variation of the Boltzmann factor $e^{(-\Delta E/kT_e)}$ can be neglected, i.e., if $\Delta E_{\text{up}} \ll kT_e$. There ΔE_{up} is the energy spread of the upper configuration, and T_e is the temperature of the electrons of the plasma, which are responsible for the populating mechanisms.

Conditions for LTE are not usually met in most high-temperature (T_e) and low-density plasmas of interest (such as in tokamaks) which are much nearer to coronal equilibrium (CE). Thus, in general, the experimental arrays may appear more or less "distorted" when compared to our formulas.

However, there are important particular cases where SWP is approximately fulfilled by the levels of the upper configuration: the cases, for highly ionized atoms in CE plasmas, when the ground configuration is nl^{N+1} and the resonant configuration is $nl^N(n+1)l'$ and decays radiatively to nl^{N+1} (mainly). In this case, the population of the nonmetastable levels of $nl^N(n+1)l'$ is governed primarily by the balance between collisional excitation from nl^{N+1} and radiative deexcitation to it, if effects of cascades from higher levels can be neglected. Taking into account the usually valid condition $\Delta E \ll kT_e$ for the energy spreads ΔE of

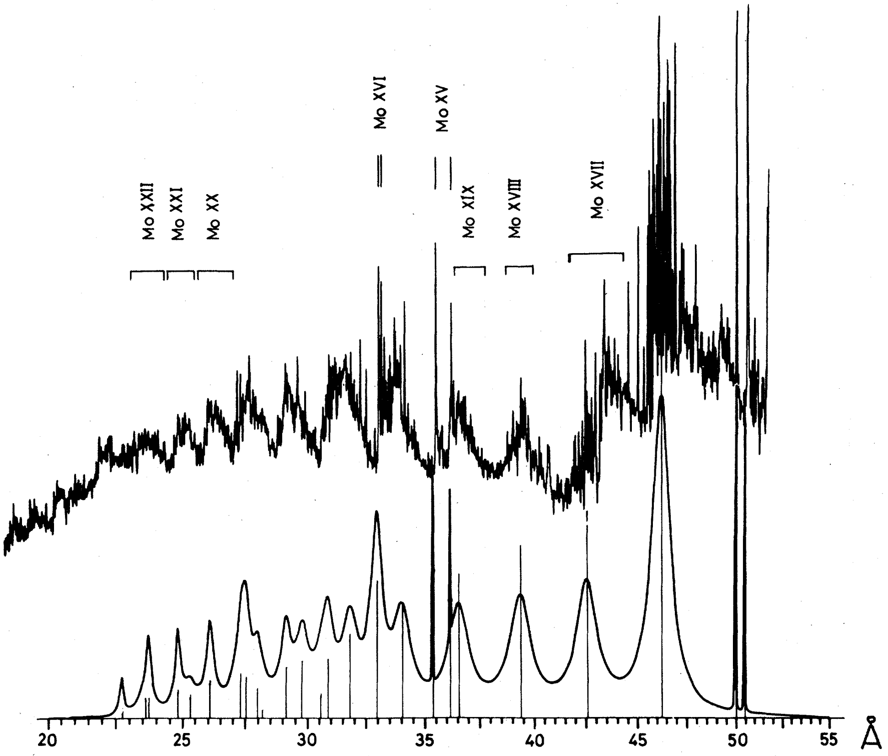

FIG. 3. Comparison between experimental (above) and theoretical (below) spectrum of Mo XV–Mo XXII. Theoretical transition arrays are $3d^{N+1}$–$3d^N4p$, $-3d^N4f$, $-3d^N5p$, $-3d^N5f$. Theoretical distributions are described here as Lorentzian, to reproduce the background of the photographic plate.

both relevant configurations, we know that excitation cross sections are approximately proportional to line strengths for allowed transitions,[28] and we derive the existence of SWP in $nl^N(n+1)l'$.

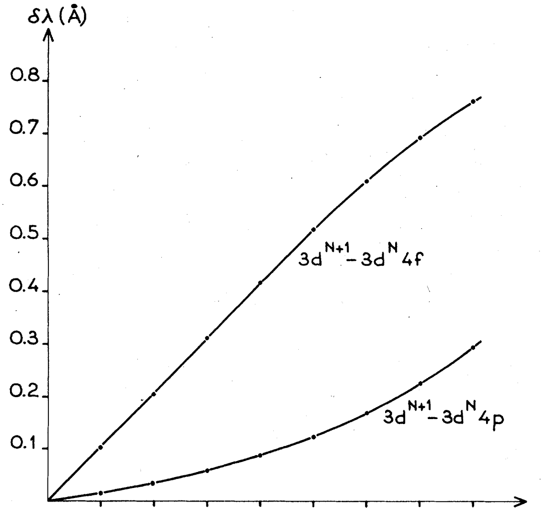

FIG. 4. Shift, in angstroms, corresponding to δE [Eq. (13)] for transitions $3d^{N+1}$–$3d^N4f$ and $3d^{N+1}$–$3d^N4p$ of Mo XVI–Mo XXIV. The curves represent the shift between the difference of the centroids of the configurations and the weighted mean of the transition arrays vs N.

This argument explains the good agreement between the formulas and the experimental spectra presented for $3d^{N+1}-3d^N4p$ in Fig. 3, although the plasma—here a vacuum spark—is not in LTE; in the same plasma conditions, other arrays, e.g., $3d^N4p-3d^N4d$, may be quite distorted. The transition arrays $3d^4-3d^34p$ and $3d^34s-3d^34p$, which have been obtained by Ekberg[17] with a sliding spark, compare also nicely[12] with our formulas.

The comparisons with experiment might be

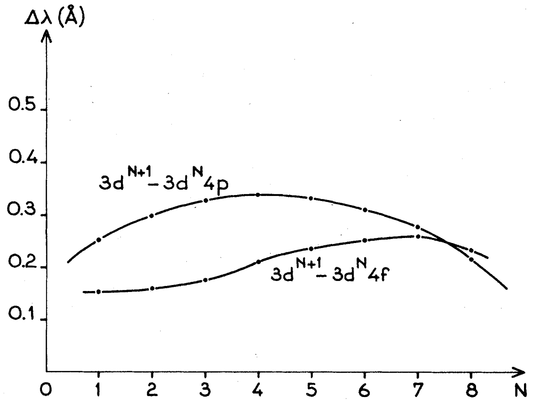

FIG. 5. Spectral width of the transition arrays $3d^{N+1}$–$3d^N4f$ and $3d^{N+1}$–$3d^N4p$ in Mo XVI–Mo XXIV, plotted vs N.

spoiled because of some other reasons.

(i) In our formulas, we use line strengths as weighting factors instead of the transition probabilities. The only difference, apart from a constant factor, lies in the ν^3 term. We have verified that the influence of the latter can be neglected in the examples we have computed.

(ii) We have supposed, right at the beginning, that there was no configuration mixing. If there were some it would obviously shift and distort the distribution of levels. Moreover, because several different electric dipole radial integrals would have to be introduced, they would not simplify out in the calculation of Eq. (4).

(iii) Another kind of approximation is involved if one uses *ab initio* values of the Slater integrals. Most *ab initio* evaluations are too large for neutral atoms, but approach the empirical values when the ionization stage goes up.

It is worth noting that approximations (i)–(iii) are valid, in particular, for highly stripped heavy atoms in hot plasmas.

Finally, our formulas are not explicitly relativistic. This is a drawback in the cases (e.g., x-rays) where one spin-orbit interaction is much larger than the Slater integrals; in that case, the spectrum would show several peaks, which we could not reproduce through the present results, which concern global distributions only. A completely relativistic treatment (*jj*-coupling scheme) would involve relativistic-configuration mixing and is outside the scope of the present study.

However, the existing data on x-ray linewidths[13, 14] suggest that there may be a contribution to the linewidths of the separate peaks, for transition elements, due to the interaction of the holes in the deep shells with the outer electrons. This would mean, in fact, that when the hole is produced, a kind of shake-up occurs which leaves the atom with a certain probability to be in any one of the possible excited states. Then, formulas akin to those of the present work might give more systematic results than previous attempts (e.g., Ref. 29) to tackle this problem.

IX. CONCLUSION

We have presented above a formalism which allows computation of the first and second moments of the distributions of energy levels and line wave numbers in atomic spectra. Two phenomena, which have been noted for many years by experimentalists, are clearly apparent. First, for some types of transitions, the mean wave number is not equal to the difference of the energy averages of the configurations. Second, the width of the transition array is, in some cases, much smaller than the widths of the configurations themselves.

This work can be helpful in all cases where the different lines of a spectrum cannot be studied separately, i.e., when all the transitions between two configurations are seen as one broad peak. For this reason we will derive more general formulas for transitions between other types of configurations, for example $l^N l'^{N'} l''^{N''}$ to $l^N l'^{N+1} l''^{N''-1}$ (some recent experimental results in plasmas of heavy atoms involve configurations with three open shells[30]). In order to extend the applicability of such a formalism, we will also consider the possibility to take into account configuration mixing and relativity.

APPENDIX: CALCULATION OF A PART OF σ^2 FOR THE TRANSITIONS BETWEEN $A = nl^{N+1}$ AND $B = nl^N n'l'$

This example is restricted to the determination of the coefficients of the products

$$F^k_{A \text{ or } B}(nl,nl)F^{k'}_{A \text{ or } B}(nl,nl)$$

in σ^2. These coefficients are denoted $C^{kk'}_{AA}(N)$, $C^{kk'}_{BB}(N)$, $C^{kk'}_{AB}(N)$, and $C^{kk'}_{BA}(N)$.

(a). It can first be shown that each of these coefficients depends on N through a polynomial whose highest power is 4. Indeed, (i) the total weight W in Eq. (4) is a multiple of $\binom{4l+1}{N}$; (ii) considering, as an example, the quantity

$$q' = \sum_{a,b} (a|G|a)(a|G|a)(a|Z|b)(b|Z|a)$$

in μ_2, it appears that the corresponding operator Op [defined in Eq. (9)] is the sum of operators acting on two, three, four, and five nl electrons, yielding contributions to q which are multiples of $\binom{4l}{N-1}$, $\binom{4l-1}{N-2}$, $\binom{4l-2}{N-3}$, and $\binom{4l-3}{N-4}$, respectively; dividing those combinatorial quantities by W shows that q' is the product of N by a polynomial in N whose highest power is 3.

It is evident that $C^{kk'}_{AA}(N) = 0$ for $N = 0$, $4l$, and $4l+1$, that $C^{kk'}_{BB}(N) = 0$ for $N = 0$, 1, and $4l+1$, and that $C^{kk'}_{AB}(N) = 0$ for $N = 0$, 1, $4l$, and $4l+1$. Therefore $C^{kk'}_{AA}(N)$, $C^{kk'}_{BB}(N)$, and $C^{kk'}_{AB}(N)$ contain, respectively, the factors $N(4l-N)(4l-N+1)$, $N(N-1)(4l-N+1)$, and $N(N-1)(4l-N)(4l-N+1)$; both $C^{kk'}_{AA}(N)$ and $C^{kk'}_{BB}(N)$ contain also an unknown binomial factor linear in N.

(b) The explicit expression of $C^{kk'}_{BB}$, for example, can be computed directly by Racah's tensor-operator methods in the simple cases $N = 2$ and $N = 4l$, which allows the complete derivation of its formula for arbitrary N. For $C^{kk'}_{AA}$, we have proven, through comparing their expressions obtained by means of Racah's methods and of the symmetry relation for coefficients of fractional parentage with respect to the half-filled shell,[31] that

$$C_{AA}^{kk'}(N) \equiv C_{BB}^{kk'}(4l - N + 1)\,.$$

As concerns $C_{AB}^{kk'}(N)$, we have written explicitly its part of highest degree in N (due to that part of Op which acts on five *nl* electrons) in the second-quantization formalism and found it exactly opposite to the analogous part of $C_{AA}^{kk'}(N)$.

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