The wave functions are those of Appendix B. The matrix elements are calculated through direct application of Eqs. (9)–(13) in Ref. 15 by formally identifying our one- and two-electron operators with his, although the operators themselves are different.[30] Finally, all integrals reduce to two types. First, there are linear combinations of the coordinates of the atoms. We have used regular hexagons for anthracene with the interatomic distance taken as the average of the measurements of Sinclair *et al.*[31] There are also integrals of the type

$$\int x^2 |\chi(\mathbf{r})|^2 d\mathbf{r}\,,$$

which are matrix elements involving the coordinates of the $2p\pi$ carbon electron about its own nucleus. For these we used the Slater functions suggested by Pariser.

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[30] There are two typographical errors in the section of Ref. 15 we use: in Eq. (11) there are two terms "$-[ij|ii]$"; one of them should be changed to read "$-[ij|jj]$". Then, in Eq. (12): $\sum_{f\neq k',l'}$ should be changed to read $\sum_{f\neq i}$.

[31] V. C. Sinclair, J. M. Robertson, and A. M. Mathieson, Acta Cryst. 3, 251 (1950).

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Theory of X-Ray Satellites

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A general theory has been developed with regard to x-ray excitations, based on the method of the sudden approximation. As one application, the production probabilities of all the normal single-hole x-ray states of F^-, Ne, Na^+, Cl^-, Ar, and K^+ have been calculated in a self-consistent-field approximation. These production probabilities have been employed for derivation of the *KL*-satellite intensity values 36.5% (F^-), 21.1% (Ne), and 14.3% (Na^+) relative to the $K\alpha_{1,2}$ line and the *KM*-satellite intensity values 39.7% (Cl^-), 26.2% (Ar), and 19.3% (K^+) relative to the $K\beta_{1,3}$ line. In calculation of the relative satellite intensities, account has been taken of the difference between the oscillator strengths of the main line and the satellites, and the decay of *KL* to the *KM* states of Cl^-, Ar, and K^+. It has further been shown that the exchange probabilities can be ignored in these calculations. The satellite intensities calculated display close agreement with the experimental intensities obtained from Deslattes's measurements as concerns Cl^- and Ar, although there is a slight disagreement in the case of K^+. It has been suggested that the usual criterion of validity for sudden approximation need not be fulfilled exactly in applications, and a connection between the sudden-approximation probability and the dipole-transition probability has been found. In conclusion, there is a discussion of solid-state effects on the satellite intensities.

I. INTRODUCTION

CONCLUSIONS with respect to the origin of x-ray satellites are almost entirely based upon calculations of the energy positions of the x-ray satellites.[1] However, in this paper, consideration is given to calculation of the relative intensity of the satellites and the main line with the aid of the sudden approximation. The change in the Hamiltonian attributable to the production of an inner vacancy or hole is then regarded as a sudden perturbation.

The possibility of treating x-ray excitation by means of the sudden approximation seems to have first been indicated by Bloch.[2] Parrat and Schnopper[3,4] have discussed the subject qualitatively in connection with the relaxation of an electron system after the formation of an inner hole. Recently, Sachenko and Demekhin[5] and the author[6] have presented some satellite-intensity calculations based upon the sudden approximation. Richtmeyer[7] studied the electron excitation of initial states of satellites in the Born approximation. This work continues the study of the sudden-approximation method, and presents the general theory with some new applications.

Related applications of the sudden approximation include calculations of auto-ionization rates of the atom in beta decay,[8–10] calculations of the shake-off rates in charge spectra induced by x rays in noble-gas atoms,[11–13]

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[1] See, for example, D. J. Candlin, Proc. Phys. Soc. (London) **A68**, 322 (1955); Z. Horak, *ibid.* **A77**, 980 (1961); R. D. Deslattes, Phys. Rev. **133**, A399 (1964).

[2] F. Bloch, Phys. Rev. **48**, 187 (1935).

[3] L. G. Parrat, Rev. Mod. Phys. **31**, 616 (1959).

[4] H. W. Schnopper and L. G. Parrat, in *Röntgenspektren und Chemische Bindung*, edited by A. Meisel (VEB Reprocolor, Leipzig, 1966), p. 314.

[5] V. P. Sachenko and V. F. Demekhin, Zh. Eksperim. i Teor. Fiz. **49**, 765 (1965) [English transl.: Soviet Phys.—JETP **22**, 532 (1966)].

[6] T. Åberg, Licenciate thesis, University of Helsinki, 1966 (unpublished).

[7] R. D. Richtmeyer, Phys. Rev. **49**, 1 (1936).

[8] A. B. Migdal, J. Phys. USSR **4**, 449 (1941).

[9] E. L. Feinberg, J. Phys. USSR **4**, 424 (1941).

[10] J. S. Levinger, Phys. Rev. **90**, 11 (1953).

[11] T. A. Carlson, Phys. Rev. **130**, 2361 (1963).

[12] T. A. Carlson and M. A. Krause, Phys. Rev. **137**, A1655 (1965).

[13] T. A. Carlson and M. A. Krause, Phys. Rev. **140**, A1057 (1965).

and derivation of the multiple electron excitation rates in Auger processes.[14]

II. THEORY

A. Probability in the Sudden Approximation of Excitation in an Arbitrary System

According to the Wentzel-Druyvesteyn theory, there exists a possibility that not only one, but two or even more photoelectrons are released from the atom in x-ray excitation. The anomalous multihole states then produce satellites, while the normal single-hole states produce the main line. The Richtmeyer theory suggests that in the anomalous states, which produce satellites, the outer electrons of the atom are excited but still bound. This theory attributes the satellite line to the simultaneous transition of an inner and an outer electron from a higher to a lower energy level, producing a single quantum. No explanation is provided in these theories of how the anomalous states arise. It is known that multihole states are produced by Auger or Coster-Kronig transitions, although one point not explained by these radiationless transitions is how the initial states of the K satellites arise.[15]

Nevertheless, it is common to both theories that some sort of anomalous state, which corresponds to an anomalous configuration of mainly the outer electrons, is responsible for a satellite line. These anomalous states can be termed "valence-electron-configuration" (VEC) states, after Parrat.[3] The basic idea, then, is that of considering the formation of an inner hole as occurring so quickly that the rapid change in the Coulombic field experienced by electrons other than the photoelectron gives rise to anomalous configurations.

Consider an arbitrary system of N electrons. If the system is in the ground state before excitation, the time-dependent wave function is

$$\psi_0(x_1,\cdots x_N)e^{-iW_0t/\hbar}, \tag{2.1}$$

in which x symbolizes the space and spin coordinate, ψ_0 is the ground-state eigenfunction of the N-electron time-independent Hamiltonian $H(N)$, and W_0 is the corresponding ground-state energy. Suppose that, in the excitation, an electron with spin ζ_i is removed from the volume element $\mathbf{r}_i$, $\mathbf{r}_i+d\mathbf{r}_i$. The new wave function of the excited system depends on the coordinate x_i, and must be a solution of the time-dependent Schrödinger equation

$$i\hbar(\partial\psi/\partial t)=H(N-1)\psi, \tag{2.2}$$

where $H(N-1)$ is the Hamiltonian of the $(N-1)$ electron system. Consequently, the solution can be written in the form

$$\psi=\mathsf{S}_n a_n(x_i)\varphi_n(x_1,\cdots x_{i-1},x_{i+1},\cdots x_N)e^{-iW_n't/\hbar}, \tag{2.3}$$

where φ_n are the eigenfunctions, and W_n' are the corresponding eigenenergies of the Hamiltonian $H(N-1)$. S_n means summation over the discrete spectra, and integration over the continuous spectra. Coordinate x_i is missing from eigenfunctions φ_n, whereas coefficients $a_n(x_i)$ depend upon the coordinate.

If it is assumed that removal of the electron occurs very quickly at $t=0$, it follows that the change $H(N)\rightarrow H(N-1)$ is almost discontinuous. Nevertheless, the wave function must, at all points in space, be a continuous function of the time at $t=0$,[16] from which it follows that

$$\psi_0(x_1,\cdots x_i,\cdots x_N)=\mathsf{S}_n a_n(x_i)\varphi_n(x_1,\cdots x_{i-1},x_{i+1},\cdots x_N) \tag{2.4}$$

for all values of x_i. Since ψ_0 is a normalizable function, and the functions φ_n constitute an orthonormal set,

$$\mathsf{S}_n\int|a_n(x_i)|^2dx_i=1. \tag{2.5}$$

Consequently, $|a_n(x_i)|^2dx_i$ can be interpreted as the probability that the system will make a transition to state n of the system of $N-1$ electrons after the removal of one electron from volume element $\mathbf{r}_i$, $\mathbf{r}_i+d\mathbf{r}_i$ with spin ζ_i. The integral

$$P_n=\int|a_n(x_i)|^2dx_i \tag{2.6}$$

is then the probability that the system will make the corresponding transition after the removal of one electron from anywhere in the system. From (2.4), the excitation probability (2.6) for an arbitrary system can be written as

$$P_n=\int\left|\int\varphi_n^*(x_1,\cdots x_{i-1},x_{i+1},\cdots x_N)\psi_0(x_1,\cdots x_i,\cdots x_N)\times dx_1,\cdots dx_{i-1},dx_{i+1},\cdots dx_N\right|^2dx_i, \tag{2.7}$$

and the following treatment is based upon this.

B. Normal X-Ray State Probability for an Atom or Ion

If Slater determinants

$$\begin{aligned}\psi_0&=\frac{1}{(N!)^{1/2}}\det(u_1,\cdots u_N),\\ \varphi_n&=\frac{1}{[(N-1)!]^{1/2}}\det(v_1,\cdots v_{N-1})\end{aligned} \tag{2.8}$$

from orthonormal spin orbitals are employed in place of the accurate wave functions in (2.7), then P_n is a

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[14] M. Wolfsberg and M. L. Perlman, Phys. Rev. **99**, 1833 (1955).

[15] For details, refer to M. A. Blochin, *Physik der Röntgenstrahlen* (VEB Verlag Technik, Berlin, 1957), p. 334; and F. R. Hirsch, Jr., Rev. Mod. Phys. **14**, 45 (1942).

[16] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 217.

product of two component probabilities $1/N$ and P' given by

$$P'=\sum_{k=1}^{N}\begin{vmatrix}\langle u_1|v_1\rangle & \cdots & \langle u_1|v_{N-1}\rangle\\ \langle u_{k-1}|v_1\rangle & & \langle u_{k-1}|v_{N-1}\rangle\\ \langle u_{k+1}|v_1\rangle & & \langle u_{k+1}|v_{N-1}\rangle\\ \langle u_N|v_1\rangle & \cdots & \langle u_N|v_{N-1}\rangle\end{vmatrix}^2, \tag{2.9}$$

where the functions u represent the ground-state spin orbitals, and the functions v represent those of the excitation state in the overlap integrals

$$\langle u_r|v_t\rangle=\int u_r^* v_t dx\,,\quad r=1,\cdots N\,,\quad t=1,\cdots N-1\,. \tag{2.10}$$

$1/N$ can be understood to be the probability that an electron is removed from a specific spin-orbital, and P' to be the probability that the remaining electrons occupy spin orbitals v after the excitation. In the central-field approximation of a free atom or ion, the overlap integral (2.10) is reduced to

$$\langle u_r|v_t\rangle=\delta_{ll'}\delta_{m_l m_l'}\delta_{m_s m_s'}\int_0^\infty R_{nl}(r)R_{n'l}'(r)r^2dr\,, \tag{2.11}$$

where $R_{nl}(r)$ and $R_{n'l}'(r)$ are the radial functions of the ground- and the excitation-state spin orbitals, respectively.

Consider the production of a normal single-hole x-ray state, which is the initial state of the main line. The angular and spin parts of the $N-1$ spin-orbitals of an atom or ion do not change in the excitation, but the radial functions change slightly due to the formation of the hole. If the radial functions did not change (frozen-structure approximation), then the excitation probability for a normal state would be 1, and no corresponding satellites should exist. This is clear if one equates $N-1$ of the spin-orbitals u with spin-orbitals v in (2.9).

It is reasonable to assume that the overlap integrals (2.11) are zero, even when only the principal quantum numbers differ. This leads to the independent-particle formula

$$P'=\prod_{nl} P(nl) \tag{2.12}$$

for the production probability of a normal state. The production probability P' is thus a product of component probabilities

$$P(nl)=\left[\int_0^\infty R_{nl}(r)R_{nl}'(r)r^2dr\right]^{2p}, \tag{2.13}$$

where p is the number of electrons in the shell. In the case of a closed shell, $p=2(2l+1)$, and in the case of a single-hole shell, $p=2(2l+1)-1$, as it is if the photoelectron escapes from a closed shell associated with the quantum number l.

Component probability $P(nl)$ can be interpreted as the probability that the electrons in shell nl stay in their orbits (keep their quantum numbers n, l, m_l, m_s) during the excitation. Thus the ratio of the probability for excitation or ionization of one or more electrons from shell nl, but from no other shells, to the probability for the normal state is

$$W(nl)=[1-P(nl)]/P(nl)\,. \tag{2.14}$$

In other words, $W(nl)$ is the relative probability for anomalous or VEC states which are the initial states of satellites corresponding to anomalous configurations of electrons originally in the nl shell. Some applications of Eqs. (2.13) and (2.14) are presented in the next section.

III. RELATIVE X-RAY SATELLITE INTENSITIES

A. Calculation of Probabilities for Normal and Anomalous X-Ray States

For calculation of the relative production probabilities for the anomalous states of a free atom or ion, both the ground-state and the normal single-hole x-ray state radial functions are required. Self-consistent-field radial functions, which agree with Hartree-Fock radial functions to a high degree of accuracy, have been calculated by Bagus[17] for F^-, Ne, Na^+, Cl^-, Ar, and K^+. The radial functions are given in terms of Slater-type orbitals, and thus the overlap integrals in (2.13) can be expressed in a closed form. Calculation of the probabilities (2.13) for these atoms and ions has been effected by using an Elliot 503 computer with a program written in ALGOL. The results are compiled in Table I for all possible normal single-hole x-ray states. The first symbol in the first column indicates the shell from which the primary photoelectron escapes, and the second symbol indicates the shell where the excitation or ionization of one or more electrons takes place when the probability $P(nl)$ is less than one.

Table I demonstrates the well-known fact that perturbation caused by the formation of a hole in a shell considerably distorts the radial functions of the electrons in the same or an outer shell, but not in one located more internally. The change in the radial functions of the outermost electrons gives rise to a considerable probability that these electrons will be subjected to excitation or ionization when an inner hole is formed.

Hereafter, consideration is confined to K states and the corresponding satellites; in these instances, the formation of anomalous states due to transitions from other anomalous states plays a minor role. The relative production probabilities of anomalous KL and KM states are presented in Table II. The notation $KL_{\rm I}L_{\rm II,III}$ or $KM_{\rm I}M_{\rm II,III}$ means simultaneous excitation or ionization of the electrons in both shells. Thus, the corresponding probability is the product of the relative probabilities $W(2s)$ and $W(2p)$ or $W(3s)$ and $W(3p)$. The

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[17] P. S. Bagus, Phys. Rev. **139**, A619 (1965).

TABLE I. Component probabilities of normal single-hole x-ray states.

State \ Atom or ion	F^-	Ne	Na^+	Cl^-	Ar	K^+
KK	0.9992	0.9993	0.9995	0.9998	0.9998	0.9998
L_{I}	0.9806	0.9816	0.9843	0.9946	0.9952	0.9958
$L_{\text{II,III}}$	0.7455	0.8365	0.8830	0.9688	0.9752	0.9764
M_{I}				0.9665	0.9701	0.9743
$M_{\text{II,III}}$				0.7427	0.8174	0.8585
$L_{\text{I}}K$	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
L_{I}	0.9971	0.9974	0.9978	0.9996	0.9997	0.9998
$L_{\text{II,III}}$	0.9134	0.9587	0.9749	0.9958	0.9965	0.9969
M_{I}				0.9798	0.9825	0.9856
$M_{\text{II,III}}$				0.7945	0.8680	0.9051
$L_{\text{II,III}}K$	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
L_{I}	0.9968	0.9964	0.9967	0.9990	0.9991	0.9992
$L_{\text{II,III}}$	0.9180	0.9576	0.9727	0.9960	0.9968	0.9975
M_{I}				0.9758	0.9789	0.9824
$M_{\text{II,III}}$				0.7951	0.8676	0.9041
$M_{\text{I}}K$				1.0000	1.0000	1.0000
L_{I}				1.0000	1.0000	1.0000
$L_{\text{II,III}}$				1.0000	1.0000	1.0000
M_{I}				0.9967	0.9972	0.9978
$M_{\text{II,III}}$				0.9259	0.9631	0.9770
$M_{\text{II,III}}K$				1.0000	1.0000	1.0000
L_{I}				1.0000	1.0000	1.0000
$L_{\text{II,III}}$				1.0000	1.0000	1.0000
M_{I}				0.9968	0.9968	0.9972
$M_{\text{II,III}}$				0.9391	0.9684	0.9797

total relative production probability for all kinds of anomalous KL or KM states is the sum of three corresponding component probabilities given in Table II.

Normal single-hole x-ray-state radial functions have been calculated in no more than a few cases. However, if the excitation or ionization of the outermost electrons owing to the formation of a hole in the K shell is considered, a useful approximation is obtainable. This well-known approximation consists in employment of the radial functions of the atom with the atomic number $Z+1$, instead of the K-state radial functions of the atom with atomic number Z. Thus, for the F^- ion, the $(Z\rightarrow Z+1)$ approximation gives the value 34.3% for $W(2p)$, which is in close accord with the corresponding value in Table II.

B. Relative Intensities of *KL* and *KM* Satellites

In this section, consideration is given to the relative intensity of the KL satellites and the $K\alpha_{1,2}$ line of neon-like ions, and of the KM satellites and the $K\beta_{1,3}$ line of argon-like ions. In both cases, we treat, by an approximation, the fact that oscillator strength f changes slightly when the outer electrons become excited or ionized. Moreover, the decay of KL states to KM states, must be taken into account with respect to the 18-electron atom or ion.

TABLE II. Relative production probabilities (%) of anomalous KL and KM states.

State \ Atom or ion	F^-	Ne	Na^+	Cl^-	Ar	K^+
KL_{I}	1.98	1.87	1.60	0.55	0.48	0.42
$KL_{\text{II, III}}$	34.14	19.55	13.26	3.22	2.55	2.42
$KL_{\text{I}}L_{\text{II, III}}$	0.68	0.37	0.21	0.02	0.01	0.01
KL	36.80	21.79	15.07	3.79	3.04	2.85
KM_{I}				3.46	3.08	2.64
$KM_{\text{II, III}}$				34.64	22.34	16.48
$KM_{\text{I}}M_{\text{II, III}}$				1.20	0.69	0.43
KM				39.30	26.11	19.55

The intensity ratio of the KL satellite group and the $K\alpha_{1,2}$ line becomes

$$\frac{I_{KL}}{I_{K\alpha_{1,2}}}=\frac{f_s}{f_0}[W(2s)+W(2s)W(2p)]+\frac{5f_p}{6f_0}W(2p), \quad (3.1)$$

in which f_0 is the oscillator strength of transitions between the normal states and f_s is the mean oscillator strength of transitions between anomalous states which correspond to excitation or ionization of L_{I}-shell electrons and L_{I}- and $L_{\text{II,III}}$-shell electrons simultaneously. Since the ionization of one electron is most probable, as will be indicated in Sec. IV B, f_s is calculated on the assumption of an initial state in which one electron is missing from both the K shell and the L_{I} shell. Correspondingly, f_p is calculated on the assumption of an initial state in which one electron is missing from the K shell and one from the $L_{\text{II,III}}$ shell. The additional factor $\frac{5}{6}$ arises because the transition probability of the $K\alpha$ line is reduced by this factor when one electron escapes from the $L_{\text{II,III}}$ shell, if Russell-Saunders coupling is supposed. The intensity ratio of the KM satellite group and the $K\beta_{1,3}$ line, in analogy with (3.1), becomes

$$\frac{I_{KM}}{I_{K\beta_{1,3}}}=\frac{f_s}{f_0}[W(3s)+W(3s)W(3p)]+\frac{5f_p}{6f_0}W(3p)+W(KL\rightarrow KM). \quad (3.2)$$

The only new feature is the correction $W(KL\rightarrow KM)$, in view of the decay of KL states to KM states.

The probabilities $W(nl)$ are given in Table II. The oscillator-strength ratios have been calculated in the frozen-structure approximation from the formula

$$\frac{f_{s,p}}{f_0}=\left[\frac{\int_0^\infty R_{1s}^-R_{np}^-r^2dr}{\int_0^\infty R_{1s}R_{np}r^2dr}\right]^2. \quad (3.3)$$

In (3.3), $n=2$ for the 10-electron case, and $n=3$ for the 18-electron case. R_{1s} and R_{np} are ground-state radial functions, and R_{1s}^- and R_{np}^- are radial functions of the ns- or np-hole normal states. The radial functions were those presented by Bagus,[17] and the ratios were calculated with the Elliot 503 computer. The results have been compiled in Table III. It should be remarked that the error induced in the oscillator strengths by the use

Table III. Ratios of oscillator strengths in accordance with Eq. (3.3).

	$n=2$			$n=3$		
Atom or ion	F^-	Ne	Na^+	Cl^-	Ar	K^+
ns hole	1.195	1.150	1.125	1.068	1.138	1.110
np hole	1.171	1.135	1.113	1.146	1.180	1.124

of the frozen-structure approximation is almost cancelled out when only the ratio of the oscillator strengths is taken into account.

In the estimation of the correction $W(KL\rightarrow KM)$, use was made of the radiative and nonradiative transition probabilities calculated by Rubenstein[18] for argon. It was assumed that the probabilities of filling the hole in the L shell are unaffected by the presence of the hole in the K shell, which again implies the employment of the frozen-structure approximation. In addition, the transition probabilities for argon were also applied in the case of the Cl^- and K^+ ions. This rather rough estimate gave the result $W(KL\rightarrow KM)=0.7\%$ for Cl^-, 0.6% for Ar, and 0.5% for K^+.

The third row of Table IV presents the results of applying Eq. (3.1) for F^-, Ne, and Na^+, and Eq. (3.2) for Cl^-, Ar, and K^+. The total correction owing to all the factors mentioned in this section is small, as can be seen by comparing the total probabilities for the KL and KM states (Table II) with the calculated relative intensities. As is indicated by the energy-position calculations of Horak[1] and Deslattes,[1] the satellite group observed on the high-energy side of the $K\alpha_{1,2}$ line of F^-, Ne, Na^+ is attributable to KL ionization states, whereas the satellite group on the high-energy side of the $K\beta_{1,3}$ line closest to the line is attributable to KM ionization states. Some relative experimental intensities of these groups can be seen in the fourth row of Table IV. Unfortunately, there are no accurate intensity measurements on F^- and Ne, but only accurate energy-position measurements made by photographic registration.[19,20] However, Moore and Chalklin[20] tried to resolve the neon $K\alpha_{1,2}$ satellite group into five components, which should exist on the assumption of Russell-Saunders coupling, and have given the relative intensities of the components. Their results indicate that the ratio of the $KL_{\mathrm{II,III}}$ and KL_{I} satellites is about 4.5, whereas theory gives about 7.

Table IV. Relative intensities (%) of satellites.

Main line		$K\alpha_{1,2}$			$K\beta_{1,3}$	
Atom or ion	F^-	Ne	Na^+	Cl^-	Ar	K^+
Theory	36.5	21.1	14.3	39.7	26.2	19.3
Experiment[a,b]			(22)	39	28	15

[a] Na^+ in NaCl, photographic registration [L. G. Parrat, Phys. Rev. **50**, 1 (1936)].

[b] K^+ and Cl^- in KCl, Ar spectra obtained by R. D. Deslattes [Phys. Rev. **133**, A390 (1964)]. Estimated error is ±2% (see the text). The experimental relative intensity of K^+ does not include the relative intensity (about 1.5%) of the $K\beta_5$ line, observed on the high-energy side of $K\beta_{1,3}$ in KCl. According to Deslattes, $K\beta_5$ is attributable to the cross transition of electrons from the $3p$ band of Cl^- filling holes in the K shells of K^+.

The estimated error included in Table IV with respect to Deslattes's measurements comprises the error made in the planimetric determination of the intensity from Deslattes's curves, the error induced by a small possible overlap of the satellites and the main line, and the uncertainties in the background. Within the limits of the estimated error, there seems to be reasonable agreement between theory and experiment for Cl^- and Ar. Against this, there exists slight disagreement for K^+, and no agreement for Na^+, where the experimental value is very uncertain as a consequence of photographic registration. Nevertheless, it should be noted that the relative intensities of Na^+, K^+, and Cl^- involve solid-state effects discussed in Sec. V.

The theory presented in this paper, together with energy-position calculations, and an assumption with respect to coupling, renders it possible to construct all the satellite-line curves, and their resultant profile relative to the main line, if some further assumptions are made about the initial states, shapes, and half-widths of the satellites. In (3.1) and (3.2), the relative intensities of two kinds of satellites are included, dependent on whether the initial states are ionization states or excitation states (bound states); it is reasonable to assume that practically all the initial states are one-electron ionization states, as will be indicated in Sec. IV.B. This will leave no more than a few lines. For example, in neon and neonlike ions there are two KL_{I} satellites of intensity ratio 1:3, and three $KL_{\mathrm{II,III}}$ satellites of intensity ratio 1:5:9, if Russell-Saunders coupling is assumed.[21] The shape of a singlet x-ray line is Lorentzian in a free atom or ion.[3] Thus the only parameters to be determined are the half-widths of the singlet components of the satellite group. If the perturbation attributable to the anomalous configurations is neglected, then the half-widths can be chosen equal to the half-width of the main line (the singlet component). It would be worthwhile to compare a resultant curve constructed in this way with an accurately recorded intensity curve corrected for instrumental factors.

IV. DISCUSSION OF THE METHOD

One important question is that of determining the range of validity of the sudden-approximation method. This has been discussed in many connections, and a short summary is given in Sec. IV B, along with a comment on the validity of the sudden approximation in the Deslattes's measurements quoted in Table IV. The partial omission of exchange made when the probability expression (2.9) is substituted by (2.12) is

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[18] R. A. Rubenstein, thesis, University of Illinois, 1955 (unpublished); results quoted in Ref. 12.

[19] F. Tyren, Nova Acta Regiae Soc. Sci. Upsaliensis **12**, 40 (1940).

[20] H. R. Moore and F. C. Chalklin, Proc. Phys. Soc. (London) **A68, 717** (1955).

[21] See, for example, Z. Horak, Ref. 1.

treated in Sec. IV A. Section IV C contains an indication of the connection between the sudden-approximation probability and the dipole-transition probability. This paper does not consider the important question of correlation effects, which are ignored when we replace the accurate wave functions with Slater determinants in Sec. II B.

A. Exchange Correction

In the free-atom case, it was assumed that the overlap integral

$$\langle u_r | v_t \rangle = \langle nlm_l m_s | n'l'm_l'm_s' \rangle = 0\,, \tag{4.1}$$

even when only the principal quantum numbers n and n' are different. Thus, in part, the exchange effects are neglected, since the use of the product of spin-orbitals instead of Slater determinants also leads to the independent-particle formula (2.12). If the spin-orbitals were Hartree instead of Hartree-Fock functions, then the exchange would be disregarded entirely.

Let us consider a specific example, the production of normal $1s$-hole states of neon. The accurate expression for probability P' is then, according to (2.9),

$$P' = \langle 1s|1s\rangle^2 \langle 2s|2s\rangle^4 \langle 2p|2p\rangle^{12} \times \left[1 - \frac{\langle 1s|2s\rangle\langle 2s|1s\rangle}{\langle 1s|1s\rangle\langle 2s|2s\rangle}\right]^2 \left[1 + \frac{\langle 1s|2s\rangle^2}{\langle 2s|2s\rangle^2}\right], \tag{4.2}$$

in which the terms involving the overlap integrals $\langle 1s|2s\rangle$ and $\langle 2s|1s\rangle$ can be interpreted as exchange probabilities. If the overlap integral $\langle 1s|2s\rangle$ is put equal to zero, then (4.2) is reduced to the independent-particle expression

$$P' = \langle 1s|1s\rangle^2 \langle 2s|2s\rangle^4 \langle 2p|2p\rangle^{12}. \tag{4.3}$$

Bagus[17] has calculated overlap integrals between the total self-consistent-field wave functions of the nl-hole states. They are all less than 10^{-2}. From his results, it can be concluded that, in (4.2), the overlap integral is at most, of order 10^{-2}. In this overlap integral, the $1s$ orbital is the ground-state orbital, and the $2s$ orbital is the normal $1s$-hole-state orbital. The overlap integral $\langle 2s|1s\rangle$ is much smaller, as the $1s$ orbital is practically the same in the different hole states. It can then be concluded that the contribution of the exchange probability is of the order of 10^{-4}, and completely negligible. Nevertheless, this does not imply that Hartree functions can be used instead of Hartree-Fock functions, but only that the exchange probability terms can be neglected. This is true for all the atoms and ions treated in this paper.

B. Validity Criteria for the Sudden-Approximation Method

According to Schiff,[22] the sudden approximation is valid when the time interval τ of the change in the Hamiltonian is less than all the periods $h/(W_m - W_n)$, where W_m and W_n are the energies of states m and n which appear when the Hamiltonian changes. According to Schnopper and Parrat,[4] this means, in the case of x-ray states, that the excitation probability can be calculated in accordance with the sudden approximation if

$$(W_{nl,n'l'} - W_{nl})\tau_{n'l'}/\hbar \ll 1\,, \tag{4.4}$$

where W_{nl} is the energy of the normal single-hole state, $W_{nl,n'l'}$ is the energy of the anomalous state with an extra $n'l'$ hole, and $\tau_{n'l'}$ is the time of transit of the ejected photoelectron past the $n'l'$ shell.

The validity criterion (4.4) is not very well satisfied in the measurements (Table IV) of Deslattes, who obtained the spectra with an excess energy of about 250 eV over threshold. For instance, in argon, the energy difference $W_{1s,3p} - W_{1s}$ is about 32 eV, and the expectation value $\langle r\rangle_{3p}$ about 0.88 Å,[23] which means that the ratio on the left-hand side of (4.4) is about 0.5. Nevertheless, an experimental study of the criterion (4.4) by Carlson and Krause[13] indicates that it is unnecessarily severe.

Carlson and Krause, with the aid of a specially designed mass spectrometer, measured the relative abundance of the differently charged ions that result from photo-ionization in the K shell of neon. From the experimental data, they evaluated electron shake-off rates, and, particularly as a function of photoelectron velocity, the extent of ejection of one $2p$ electron which follows the formation of the hole in the K shell. Their findings indicate that the shake-off probability of the $2p$ electron increases rapidly above the energy limit for simultaneous ionization of a $1s$ and a $2p$ electron, and attains a saturation value of 15.8% when the ratio in (4.4) is still about 0.4.[24] The saturation value is in close agreement with the sudden-approximation value of 14.9% calculated on the assumption that all VEC states are ionization states.[25] Their results further indicate that the difference of 1.4% between the total probability $1 - P(2p)$ and the one-$2p$-electron ionization probability is almost entirely attributable to two-$2p$-electron ionization. Thus, it can be concluded that excitation to discrete VEC states with bound electrons is negligible, at least when the ratio in (4.4) is less than 0.4, and that the VEC states are mostly one-electron ionization states, in agreement with the theory.

C. Connection between Sudden-Approximation Probability and Dipole-Transition Probability

Let us consider x-ray excitation by means of the usual time-dependent perturbation theory of the atom in a

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[22] Reference 16, p. 218.

[23] This value has been calculated by Bagus, Ref. 17.

[24] Carlson and Krause give a value of 0.2, but use the ionization energy of NeI instead of the energy difference $W_{1s2,\mathrm{p}} - W_{1s}$.

[25] Carlson and Krause also made use of the radial functions of Bagus in their calculations, and give the corresponding value of 15.1%.

radiation field. If the x-ray state is a state in the continuum, which means that the photoelectron has been ejected from the atom with kinetic energy, then the dipole-transition probability per unit energy is proportional to derivative df/dW of the oscillator strength f. The derivative is given by

$$\frac{df}{dW}=\frac{2m}{3\hbar^2}W|\langle\psi|\sum_{j=1}^{N}\mathbf{r}_j|\psi_0\rangle|^2, \tag{4.5}$$

where excitation energy W is the sum of the x-ray-state energy and the kinetic energy of the photoelectron. ψ_0 is the ground-state wave function, and ψ the x-ray-state wave function, also dependent upon the coordinate of the photoelectron. ψ is normalized per energy interval.

Assume that Slater determinants are employed instead of accurate wave functions in (4.5). The Slater determinant which represents the x-ray state is now of order N, and includes a spin-orbital $v(W,l,m_l,m_s)$ belonging to the continuum. Thus, in the case of excitation to the normal $1s$-hole state of neon, the derivative of the oscillator strength becomes

$$\frac{df}{dW}=\frac{2m}{3\hbar^2}W\langle 1s|1s\rangle^2\langle 2s|2s\rangle^4\langle 2p|2p\rangle^{12}\left[1-\frac{\langle 1s|2s\rangle\langle 2s|1s\rangle}{\langle 1s|1s\rangle\langle 2s|2s\rangle}\right]^2$$
$$\times\left|\left[\langle 1s|\mathbf{r}|v\rangle+\frac{\langle 2p|v\rangle}{\langle 2p|2p\rangle}\langle 1s|\mathbf{r}|2p\rangle+\frac{\langle 1s|2s\rangle}{\langle 2s|2s\rangle}\langle 2s|\mathbf{r}|v\rangle+\frac{\langle 1s|2s\rangle\langle 2p|v\rangle}{\langle 2s|2s\rangle\langle 2p|2p\rangle}\langle 2s|\mathbf{r}|2p\rangle\right]\right|^2, \tag{4.6}$$

when the dipole selection rules are taken into account. Thus, df/dW is proportional to P' given by (4.3), and defined previously in the sudden-approximation method as the production probability of the normal $1s$-hole state.

If the overlap integral $\langle 1s|2s\rangle$ is ignored, as in Sec. IV.A, and, further, if the overlap integral between the outermost core orbital and the photoelectron orbital $\langle 2p|v\rangle$ is put equal to zero, then, from (4.6),

$$\frac{df}{dW}=\frac{2m}{3\hbar^2}WP'|\langle 1s|\mathbf{r}|v\rangle|^2. \tag{4.7}$$

The dipole-transition probability is accordingly proportional to the product of the normal-state probability P' and a probability that an electron is removed from the K shell into the continuum. This result holds generally for any normal single-hole state if the exchange and the interaction between the photoelectron and core electrons are ignored, as is also the case in the sudden-approximation method.

V. SOLID-STATE EFFECTS

So far, consideration has been confined to calculations of x-ray satellite intensities of free atoms and ions with closed shells, but the extension of the method to atoms and ions with nonclosed shells is obvious. A further restriction is that the treatment concerns only satellites with initial states which correspond to a hole in the K shell and one or more holes in the outermost shells, since the effect of decay of other anomalous states to these states is small. However, these satellites are sensitive to the crystal environment of the atoms and ions, as is demonstrated by the following examples of two recent measurements.

The agreement between theory and experiment as regards the crystal KCl (Table IV) indicates that the free-ion picture works quite well for KCl; this does not apply to all the chlorides. A measurement of the $K\beta$ spectra of chlorine in the chlorides by Vainshtein, Mazalov, and Zyryanov[26] indicates that the relative intensities of the $K\beta_{1,3}$ satellites in crystals of NaCl and RbCl are about the same as in KCl, but not in crystals of LiCl and AgCl, where the satellites are stronger than the main line. This interpretation assumes that the satellites are on the high-energy side of the main line. A measurement made by Baun and Fischer[27] points to a change in the peak intensities of different members of the $K\alpha_{1,2}$ satellites in magnesium, aluminium, and silicon when these elements oxidize. The most radical change occurs in going from metallic aluminium to oxide; the total peak intensity of the $K\alpha_{1,2}$ satellite group increases by about 15%, and the line ratio of the two strongest members of the group doubles.

In principle, the relative satellite intensities of an arbitrary solid can be treated by proceeding from the general probability formula (2.7) if the excitations are sufficiently sudden. However, it seems preferable to calculate the relative satellite intensities of the free atom first, and then attempt to incorporate solid-state effects as perturbations. It is felt that this is possible, as, according to (2.12) and (2.13), the relative satellite intensity depends very simply upon the radial functions of the outermost shell spin orbitals, which are most sensitive to the crystal environment. A study of the solid-state effects is in progress.

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[26] É.E. Vainshtein, L. N. Mazalov, and V. G. Zyryanov, Fiz. Tverd. Tela **7**, 1099 (1965) [English transl.: Soviet Phys.—Solid State **7**, 882 (1965)].

[27] W. L. Baun and D. W. Fischer, in *Advances in X-Ray Analysis*, edited by W. M. Mueller, G. R. Mallet, and M. J. Fay (Plenum Press, Inc., New York, 1965), Vol. 8, p. 371.