

Heavy alkali atoms in jellium

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We report one-electron calculations of the soft-x-ray outer-shell absorption and emission in K, Rb, and Cs. The absorbing ion is placed at the center of a metal consisting of a valence band of electrons and a uniform positive background which has a spherical cavity removed from around the ion. Self-consistent solutions for states with and without a core hole are found using the density-functional approach. In our solution the core electrons bound to the central ion and the valence electrons are allowed to relax into the self-consistent solution. We find self-consistent potentials, charge densities, threshold energies, and cross sections for the soft-x-ray transitions. Moreover, we calculate the exponents α , α_0 , and α_1 essential to the threshold theory of Mahan, Nozières, and de Dominicis. We point out that the anomalous behavior of α_0 for K, Rb, and Cs, where it decreases for increasing r_s rather than increases as it does for other metals, can be explained if one takes into account the effects of the structure and size of the core hole, as well as the screening when determining α_0 for a series of metals.

I. INTRODUCTION

For many metals the x-ray absorption and emission spectra near threshold show deviations from the expected one electron form. The spectra at the edge are not step functions but instead are either rounded or singular. Mahan¹ has shown that the many electron reaction to the sudden creation of a core hole modifies the one-electron form of the spectra near threshold. He found that it follows a power law. Nozières and de Dominicis² have shown that the form of the power law is

$$\sigma_l(\epsilon) = A_{l+1}(\epsilon) \left| \frac{\epsilon - \epsilon_{th}}{\xi} \right|^{-\alpha_{l+1}} + A_{l-1}(\epsilon) \left| \frac{\epsilon - \epsilon_{th}}{\xi} \right|^{-\alpha_{l-1}}, \quad (1)$$

where l is the angular momentum of the core level, dipole selection rules restrict transitions to states where l changes to $l \pm 1$, ϵ_{th} is the threshold energy, and $A_{l\pm 1}(\epsilon)$ is the single particle spectrum. They predicted that the exponents should have the form

$$\alpha_l = (2/\pi)\eta_l(\epsilon_F) - \alpha, \quad (2)$$

$$\alpha = 2 \sum_l (2l+1) [\eta_l(\epsilon_F)/\pi]^2, \quad (3)$$

where $\eta_l(\epsilon_F)$ is the phase shift of an electron at the Fermi level with angular momentum l scattered by the screened potential turned on when the core hole is created or destroyed. When α_l is positive the spectrum has a singularity at threshold. When α_l is negative the spectrum is rounded. Thus the many body theory is capable of explaining both types of behavior near threshold.

Much work has been done to test this explanation both experimentally and theoretically. However

much of the experimental focus has been on Li, Na, Mg, and Al. As a result, this has been the primary focus of the theoretical activity as well. Two distinct types of theoretical calculations of these exponents have been done. Originally³⁻⁷ some form of a screened Coulomb potential or a pseudopotential was used for the core hole potential to determine phase shifts. Recently two similar calculations have been performed in which no assumption was made about the form of the core hole potential. Instead, the effect of the core hole potential was determined by using the density functional method to find self-consistent potentials for the system with and without a core hole. One of the calculations was done by Almladh and von Barth.⁸ The other was done by Mahan and the author.⁹ In that paper, hereafter referred to as I, the similarities and differences between these two calculations were discussed. Both calculations were able to predict threshold energies and in I one-electron absorption cross sections were calculated for Mg and Al which agree qualitatively with experiments. In both papers exponents were calculated which agree fairly well with experimental values. There is a problem, however, with comparing theoretical predictions with experimental values. Edge spectra are affected by phonon contributions, lifetime broadening, density of states features, and matrix element effects as well as the many body effects. It is often difficult to separate these effects. In fact the exponents taken from some data appear to be inconsistent with various restrictions, such as the Friedel sum rule, that can be placed on the phase shifts.¹⁰ This has cast doubt on the importance of the many body effects, so it is important that as many metals as possible be tested.

Until recently the observations of the emission spectra of potassium^{11,12} had not been detailed enough to show an edge singularity. However Norris¹³ and Crisp¹⁴ have now both presented experimental evidence that the edge singularity exists in the $M_{2,3}$ spectra of K. Edge singularities have also been seen in the soft-x-ray absorption spectra of the heavy alkali metals K, Rb, and Cs by Ishii and coworkers.¹⁵ Unfortunately only Ishii has been able to determine values for the exponents α_0 .

From analysis of data for Na, Mg, and Al, Dow and Sonntag¹⁶ found that the relation $\alpha_0 = 0.068r_s$, where r_s is the electron gas parameter, fits the data. The monotonic increase in α_0 with increasing r_s is an effect of screening. As r_s increases, screening is less effective and so the screened core hole potential is more attractive. Because the scattering increases, α_0 increases as well. However Ishii has found that the α_0 of K, Rb, and Cs not only are too small to fit the empirical rule but they decrease with increasing r_s . This anomalous behavior of the α_0 for these metals certainly appears to support evidence casting doubt on the importance of many body effects.

In this paper we present the results of an application of the model presented in I to study the x-ray transitions in K, Rb, and Cs. In Sec. II we briefly describe the model. In Sec. III we present the results. We first describe tests we made of the model on free ions with 18, 36, or 54 electrons. We find that threshold energies are adequately described by the model but that the one-electron cross sections for absorption in these ions are not accurate because important correlation effects are left out of the wave functions. We present our results for metallic K, Rb, and Cs for charge densities, potentials, cross sections, phase shifts, and exponents. We calculate α_0 which agree neither with experiment nor with the empirical rule. The discrepancy with the experimental values appears to be due to the difficulty of separating out the many contributions to the edge spectra plus whatever uncertainty there is due to the simplicity of our model. The applicability of the empirical rule to metals other than those it was fitted to is based on the assumptions that core hole structure is not important in determining the phase shifts and that only the changes in screening when r_s changes cause variations in α_0 . We find for low electron density metals like K, Rb, and Cs that the core hole structure is important and that, as r_s varies, the effect of the core hole structure on the phase shifts and exponents competes against the effect of screening. When there is little screening we expect the effects of the core hole structure to be dominant. We give this as an ex-

planation of the anomalous behavior of α_0 for K, Rb, and Cs and conclude that this anomalous behavior does not support evidence that many body effects are not important for the x-ray edge problem.

II. THE MODEL

The model we use to study soft-x-ray transitions is carefully described and justified in I. Here we will only briefly review its features. The simplest model one can use for a metal is the jellium model where the positive ions of the metal lattice are treated as a uniform positive background and there is a valence band of electrons which neutralizes the background. Since we are studying x-ray transitions that occur at a particular ion we want a realistic model of that ion's environment. We start with a jellium metal with the density of the background and valence band appropriate for the metal under consideration (see Table I for the free-electron parameters used). In the center of the positive background we create a spherical vacancy with radius R_{WS} , the Wigner Seitz radius, and at the center of this cavity we put the nuclear charge Z (for example, 19 for K). This background plus the cavity and the nucleus determine a potential which we use when finding, self-consistently, the wave functions of the electrons bound to the central nucleus and electrons in the valence band.

We calculate these wave functions by using a single particle equation determined by the density-functional method^{17,18}

$$\left(-\nabla^2 - \frac{2Z}{r} - 2 \int d^3r' \frac{[n(\vec{r}') - \rho(\vec{r}')] }{|\vec{r} - \vec{r}'|} + V_{ex}[\rho(\vec{r})] + V_{cor}[\rho(\vec{r})] \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \quad (4)$$

where $n(\vec{r})$ is the charge density of the positive background $n(\vec{r}) = k_F^3/3\pi^2$, if $r > R_{WS}$, $n(\vec{r}) = 0$, if $r < R_{WS}$, and $\rho(\vec{r})$ is the electron density

$$\rho(\vec{r}) = \sum_{\text{bound states}} |\psi_i(\vec{r})|^2 + \sum_{\text{valence states } \epsilon < \epsilon_F} |\psi_i(\vec{r})|^2. \quad (5)$$

When we calculate the charge density of the ground

TABLE I. Free-electron parameters of the jellium model. The Fermi momentum is k_F , the Fermi kinetic energy ϵ_F , the Wigner-Seitz radius R_{WS} , and the electron gas parameter r_s .

	$k_F (a_0^{-1})$	ϵ_F (Ry)	$R_{WS} (a_0)$	$r_s (a_0)$
K	0.397	0.158	4.86	4.86
Rb	0.360	0.130	5.33	5.33
Cs	0.339	0.115	5.66	5.66

state we sum over those bound states with the smallest energy eigenvalues which are needed to fill the occupied levels. For the system with a core hole we sum over one less outer level p state. The valence state sum is made assuming a free-electron density of states. For the heavy alkali metals this is a good approximation when there are no core holes. Even with a core hole the range of the screened core hole potential is short and so we can ignore any change in the density of states. $V_{\text{ex}}(\rho)$ is the Kohn-Sham local density exchange potential¹⁹ and $V_{\text{cor}}(\rho)$ is the Wigner correlation potential.²⁰ As discussed in I we must correct Eq.

(4) when we find bound states to eliminate self-interaction effects which are big for localized states. We do this for bound states by eliminating from the Coulomb potential the self-interaction contribution of the bound state we are studying. By solving Eq. (4) for each electron state and using Eq. (5) in determining the potential we get self-consistent wave functions for both the bound and valence electrons.

Using the energy functional of the density functional method and Eq. (4) we find the following expression for the total energy of the system:

$$E(\rho) = \sum_{\text{bound states}} \epsilon_i + \sum_{\text{valence states } k < k_F} \int k^2 |\psi_k(\vec{r})|^2 d^3r + 2Z \int d^3r \frac{n(\vec{r})}{r} + \int \frac{[n(\vec{r}) - \rho(\vec{r})][n(\vec{r}') + \rho(\vec{r}')]}{|\vec{r} - \vec{r}'|} d^3r d^3r' - \int \frac{\delta}{\delta \rho} \{ \epsilon_{\text{ex}}[\rho(\vec{r})] + \epsilon_{\text{cor}}[\rho(\vec{r})] \} \rho(\vec{r}) d^3r + 2 \sum_{\text{bound states}} \int \frac{|\psi_i(\vec{r})|^2 |\psi_i(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d^3r d^3r', \quad (6)$$

where ϵ_{ex} and ϵ_{cor} are the exchange and correlation energy per particle. By first calculating the total energy for states with and without a core hole and then taking the difference in the two energies we obtain the threshold energy for x-ray absorption and emission.

We also calculate the one body emission and absorption spectra. We compute the dipole approximation to the matrix element using the length form. The cross section for a transition with the excited electron changing its angular momentum from l to $l \pm 1$ is

$$\sigma_{I \rightarrow I \pm 1} = C_{I \pm 1} \frac{\xi \hbar \omega}{k} \left| \int r^3 dr \psi_{k, I \pm 1}(r) \psi_{n, l}(r) \right|^2 \delta(\epsilon_k + \epsilon_{\text{th}} - \hbar \omega). \quad (7)$$

ϵ_{th} is the threshold energy, $\hbar \omega$ the photon energy, ϵ_k the energy relative to the Fermi level of the excited electron, and ξ the overlap of the remaining electrons (about 0.95 for free ions but taken to be unity for metals). $\psi_{n, l}$ is the radial wave function for the bound state and $\psi_{k, l}$ is the radial wave function for the continuum state with momentum k . It has the asymptotic form

$$\psi_{k, l} \xrightarrow{r \rightarrow \infty} \left(\frac{1}{r} \right) \sin \left(kr + \delta_l(k) - \frac{l\pi}{2} \right)$$

in metals,

$$\psi_{k, l} \xrightarrow{r \rightarrow \infty} \left(\frac{1}{r} \right) \sin \left(kr - \frac{l\pi}{2} + \frac{Q}{k} \ln(2kr) + \eta_l + \delta_l(k) \right),$$

for free ions, where $\eta_l = \arg[\Gamma(l+1 - iQ/k)]$, Q is the net charge on the ion and $\delta_l(k)$ is the phase

shift. $C_{I \pm 1}$ is a constant which includes the contribution from the integration over angles.²¹

In both emission and absorption calculations the bound state is the outer s or p state in the system without a core hole. However there are two approximations that can be made for the excited electron state. One can use continuum states of either the system in its ground state (the ground state approximation) or the system with a core hole (the excited state approximation). In I we found that the latter approximation worked best for absorption near threshold where the outgoing electron is slow and should experience the potential of the fully relaxed system with a core hole. However, the first approximation was slightly better at higher energies when the electron stays near the excited ion only a short time and the perturbation due to the core hole has less effect. To calculate emission cross sections in I we used the valence electron wave functions of the system with a core hole (the initial state of the emission process). This gave low energy resonances not seen in experimental data. Many calculations of emission²² have been done using ground-state wave functions found from band-structure calculations for the valence states. These exhibit none of the resonant behavior seen in our calculations. We do the emission calculations in both approximations to check these results.

III. RESULTS

We first tested our method by calculating the x-ray absorption cross sections and threshold energies of closed shell ions with 18, 36, or 54

TABLE II. Calculated and experimental $3p$ threshold energies for photoionization from the indicated free ion ground states. The Ar $3s$ threshold is also included. The experimental values, E_{exp} , are taken from the work of Moore and Samson (Refs. 23–25).

Rydbergs	Cl ⁻	Ar	K ⁺	Ca ²⁺	Sc ³⁺	Ar(3s)
E	0.27	1.16	2.32	3.73	5.39	2.20
E_{exp}	0.27	1.16	2.34	3.77	5.43	2.15

electrons for transitions when an outer level p electron is excited to the continuum. We did a similar calculation in I for ions with 10 electrons and were able to predict threshold energies with 0.01 or 0.02 Ry accuracy. For the Cl⁻, Ar, K⁺, Ca²⁺, and Sc³⁺ ions with 18 electrons we obtain similar agreement for the $3p$ threshold energies and nearly as good agreement for the $3s$ threshold of Ar. These results are shown in Table II. The error is greatest for the ion with the highest net charge. Moreover the theoretical values are less than the experimental values. The Wigner form for the correlation energy is not accurate at high electron density. At these densities the Gell-Mann Brueckner form²⁶ is more accurate and it makes a larger contribution. Using an interpolation between these two forms, as done by Tong and Sham,²⁷ we might not underestimate the contribution of correlation for ions with a large net charge.

The results for the heavier ions, with 36 or 54 electrons, are shown in Table III. Measurements of the threshold energies of Sr²⁺, Y³⁺, and La³⁺ have not been made so only upper and lower bounds are given. Again, the error is only 0.01–0.02 Ry for most of these ions. The largest error occurs for Cs⁺. This error is much larger than those for I⁻, Xe, or Ba²⁺ and has the opposite sign. In view

TABLE III. Threshold energies for transitions from the outer p states of the indicated free ions. The E_{exp} are the experimental values taken from the work of Moore (Refs. 23 and 24). Experimental results for Sr²⁺, Y³⁺, and La³⁺ are incomplete and only upper and lower bounds are given.

Rydbergs	E_{exp}	E
Br ⁻	0.25	0.26
Kr	1.03	1.04
Rb ⁺	2.02	2.02
Sr ²⁺	0.81 < E_{exp} < 4.2	3.15
Y ³⁺	1.51 < E_{exp} < 5.7	4.46
I ⁻	0.23	0.25
Xe	0.89	0.92
Cs ⁺	1.85	1.74
Ba ²⁺	2.61	2.66
La ³⁺	1.4 < E_{exp}	3.70

of the better agreement for the other ions, the error for Cs⁺ is quite anomalous. The experimental value for Cs⁺ (Ref. 28) was measured forty years ago. It possibly is in error.

For the heavier ions we should also consider including relativistic corrections although we have made no attempt to do so. Although there is no exact way of including the relativistic corrections for a many electron system, several approximate calculations²⁹ have been done. For ions with ten electrons, the relativistic correction³⁰ to the energy level of a $1s$ state is about 0.3 Ry, for a $2s$ state about 0.03 Ry and for a $2p$ state about 0.01 Ry. The relativistic corrections lower the energy levels so they should increase the threshold energy. In the heavier ions the relativistic correction can lower the energy of the inner levels by 5–10 Ry. However the change in the outer p level is still 0.05 Ry or less. Thus our threshold calculations should be meaningful even without the relativistic corrections.

We have calculated the absorption cross sections for these ions in both the ground state and the excited state approximations. However, we can compare results only for atoms because the cross sections for the ions have not been observed. We present the results for Ar (see Fig. 1). The results and discussion for Kr and Xe are similar. Although the one electron picture gives an adequate description for the x-ray absorption of Ne it does not work well for Ar for photoionization of $3p$ electrons. We get no agreement near threshold for Ar. The excited state cross section has approximately the correct value at threshold but it does not have the maximum away from threshold. With the ground state approximation we get a threshold value which is too small and a maximum which is too large. This poor agreement near threshold is to be expected. Correlation effects in the wave function and multielectron excitations are more important near threshold for Ar than for Ne. Hartree-Fock calculations³¹ and other one body calculations^{32,33} are not significantly better than our calculation. Including intrachannel correlations for the ejected electron³² improves the results. However, a thorough treatment of correlations and final-state excitations^{34,35} is needed to reproduce qualitatively the shape of the cross section. Away from threshold, where the electron has a higher kinetic energy and should be affected less by correlation, the agreement is much better.

The matrix element calculated for the absorption cross section of Ar is an overlap between a $3p$ core level and a continuum level weighted by a factor of r . Since the $3p$ core level has a much larger extent than a $2p$ level, this factor of r gives a larger contribution for Ar than for ions

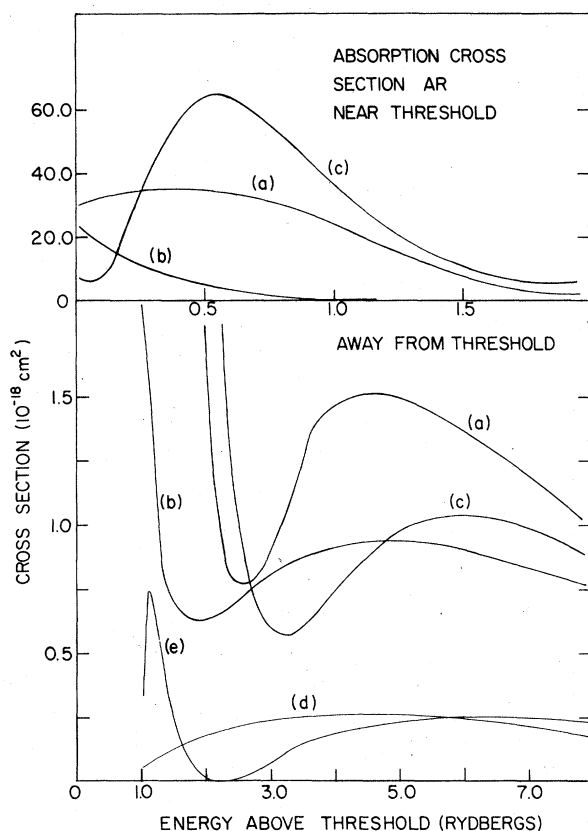


FIG. 1. Experimental data and theoretical calculations for the x-ray absorption cross section of Ar atoms: (a) the experimental data of Samson (Ref. 25), (b) the $3p \rightarrow d$ plus $3p \rightarrow s$ cross section using the excited-state approximation, (c) the $3p \rightarrow d$ plus $3p \rightarrow s$ cross section using the ground-state approximation, and the $3s \rightarrow p$ cross section using (d) the excited-state approximation, and (e) the ground-state approximation.

with outer $2p$ shells. In addition the $3p$ level has one node and so there is large cancellation in the overlap integral. This makes the matrix element much more sensitive to changes in the wave function of the excited electron. In fact the overlap integral for the $3p$ to d transition is negative for excitation energies near threshold where the $3p$ to d cross section has its first peak. The overlap integral goes to zero at the energy where the $3p$ to d cross section goes to zero and becomes positive at higher energies. If the potential used to calculate the continuum states were made more attractive, a continuum state would have its first node closer to the nucleus and the zero of the overlap integral would occur at a lower energy. This might greatly change the form of the cross section. Because of this sensitivity to the continuum wave function, cross sections for ions with $3p$ electrons in the outer shell are more difficult to calculate in the one electron approximation than

those for ions with $2p$ electrons in the outer shell. Similar problems occur for ions with $4p$ or $5p$ electrons in the outer shell.

Because we have trouble describing the absorption cross sections of Ar, Kr, and Xe using a single particle description, we should be nervous about ignoring correlation in the wave function when we study metallic K, Rb, and Cs. Admittedly we should not expect to calculate reasonable cross sections. However, the threshold energies we calculated for the free ions were not sensitive to the lack of correlation in the wave functions so we should expect to have no problem with our threshold calculations for the heavy alkali metals. In addition we calculate the phase shifts for scattering in each metal with and without a core hole present. These should not be as sensitive to correlation effects as the overlap integrals are. Moreover, we are primarily interested in calculating the edge exponents. They depend on the differences between phase shifts for electrons in the ground state and the core hole state. We expect the neglect of correlation to be less important when we take these differences. Finally, since we consider a metal, the correlation effects between a conduction electron and a particular ion should be smaller than in the free ion case where there is only one ion and no screening.

We obtain self-consistent solutions for both the states with and without a core hole for each metal. In all cases the Friedel sum rule,³⁶

$$Q = \frac{2}{\pi} \sum_l (2l+1) [\delta_l(\epsilon_F) - \delta_l(0)] \quad (8)$$

is satisfied where Q is the excess charge to be screened and the δ_l are the phase shifts of valence electrons at the Fermi level and at the bottom of the valence band. This insures the charge neutrality of each state. The radial charge density in K of the bound electrons and the excess valence electrons [$4\pi r^2(\rho_v(r) - \rho_0)$ where $\rho_v(r)$ is the valence electron density and ρ_0 is the density of the unperturbed band] is plotted in Fig. 2. In the system with a core hole the extra electron is found just outside the core hole. However, in the heavy alkalis the core hole is not screened as quickly as in Li, Na, Mg, and Al. In I we found that the ratio of the position of the maximum in the screening charge density to the Wigner Seitz radius was 0.65 for Al, 0.68 for Mg, 0.73 for Li, and 0.79 for Na. For K it is 0.83, for Rb, 0.84 and for Cs, 0.93. This is to be expected since the electron density of each of the heavy alkali metals is less than that of the lighter metals. In addition, in K the charge density near the origin has one more oscillation than the charge densities of Na, Mg, and Al have. This reflects the fact that the valence electrons in

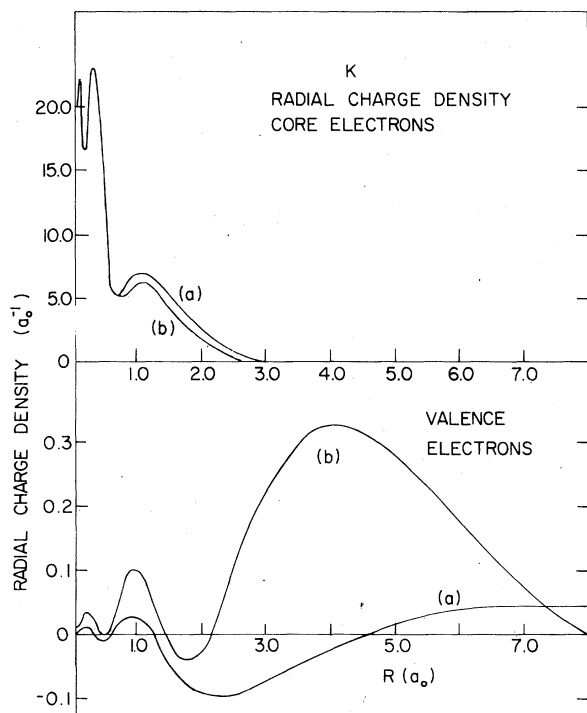


FIG. 2. Radial charge density of the core electrons and the excess valence electrons in K: (a) for the ground state, and (b) for the state with a $3p$ core hole. Note the change in scale for the core and valence electrons. R_{WS} is $4.86a_0$.

K are $4s$ and $4p$ electrons with one extra node. Similarly, these are even more extra nodes in the charge densities of Rb and Cs.

Using the self-consistent charge densities found for the ground states and the core hole states and Eq. (6), we calculated the energy of each state for each metal. The difference in the two energies for a particular metal is the threshold energy for that metal. Our results are shown in Table IV. The results agree very well with the experimental observations.^{13,14,37} This agreement is even better than the agreement we got in I for the threshold

TABLE IV. Experimental and theoretical values for threshold energies: (a) experimental results for K (Refs. 13 and 15) and for Rb and Cs (Refs. 15 and 37), and (b) our calculations.

Rydbergs	(a)	(b)
K	1.35	1.33
Rb	1.10	1.06
Cs	0.87	0.84

energies of Li, Mg, and Al. The result for metallic Cs is much more accurate than the value for the Cs^+ ion. This lends credence to our earlier suggestion that the experimental threshold of Cs^+ is in error.

In solving Eq. (4) for the valence electron wave functions we determine the phase shifts for the valence electrons. In Table V we list the phase shifts for the states at the bottom of the valence band and the change in phase shift between the Fermi level and the band bottom. The phase shift at zero energy is either zero or a multiple of π . For each multiple of π the wave function has one more node than the same wave function for a free electron. The s electrons of K have three extra nodes indicating their $4s$ character. The p waves of K have two extra nodes showing $4p$ character and the higher waves of K have no extra nodes. These are the characteristics of the lowest unfilled orbitals of a K^+ ion. The results for Rb and Cs are similar.

A comparison of the phase shifts for electrons in Mg, Al, and the heavy alkali metals indicates the effects that screening and the structure of the core hole have on the scattering. In Fig. 3 we plot the differences between the phase shifts for electrons in the systems with and without a core hole as a function of wave vector k . In Fig. 4 we plot the screened core hole potentials of Mg, Al, K, and Cs (the screened core hole potential is taken to be the difference between the self-consistent potentials of the system with and without a core hole). The differences in phase shift plotted

TABLE V. Phase shifts and Friedel sums for the ground states and core hole states of the heavy alkalis. δ_l is the phase shift at zero wave vector. $\Delta\delta_l$ is the difference between the phase shifts at the Fermi level and at zero wave vector. FS is the Friedel sum.

	δ_0	$\Delta\delta_0$	δ_1	$\Delta\delta_1$	δ_2	$\Delta\delta_2$	FS
K ground state	3π	-0.181	2π	-0.013	0.0	0.044	0.0000
K $3p$ core hole	3π	0.451	2π	0.231	0.0	0.102	1.0000
Rb ground state	4π	-0.145	3π	-0.031	π	0.051	-0.0045
Rb $4p$ core hole	4π	0.496	3π	0.205	π	0.112	0.9942
Cs ground state	5π	-0.254	4π	-0.054	2π	0.090	-0.0027
Cs $5p$ core hole	5π	0.235	4π	0.086	2π	0.245	1.0001

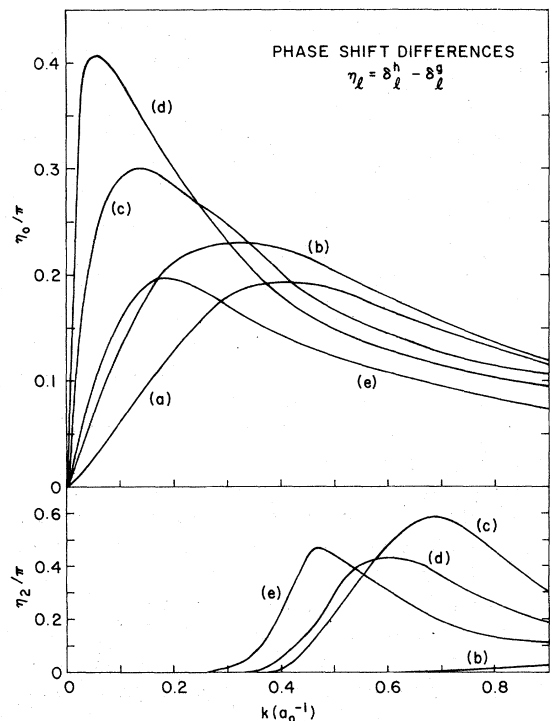


FIG. 3. The differences η_i between the phase shifts δ_i^h and δ_i^g for, respectively, the state with and without a core hole for: (a) Al, (b) Mg, (c) K, (d) Rb, (e) Cs. The results for Al and Mg are taken from I. The η_2 for Al is too small to be shown.

in Fig. 3 are the changes in phase shift which occur when the screened core hole potential is added to the ground-state potential and this potential for the system with a core hole is used to calculate the phase shifts. These phase shift differences are the same as the phase shifts calculated using just the screened core hole perturbation only in first-order Born approximation. However, an exact relationship³⁸ does exist between the differences and the screened core hole potential. If we denote the phase shifts and the self-consistent potential of the system with a core hole by δ_i^h and V_h and those for the system without a core hole by δ_i^g and V_g , then

$$\sin(\delta_i^h - \delta_i^g) = -\frac{2m}{\hbar^2 k} \int_0^\infty Y_i^g(V_h - V_g) Y_i^h dr.$$

Y_i^h and Y_i^g are the regular solutions for wave vector k of the radial wave equation in the systems with and without a core hole. In our case the $\delta_i^h - \delta_i^g$ are the differences plotted in Fig. 3 and $V_h - V_g$ is the screened core hole potential.

The large k differences in phase should be sensitive to the core hole potential at small distances. This is evident in Fig. 3. The differences in s -phase shift are larger at large k for Al and Mg

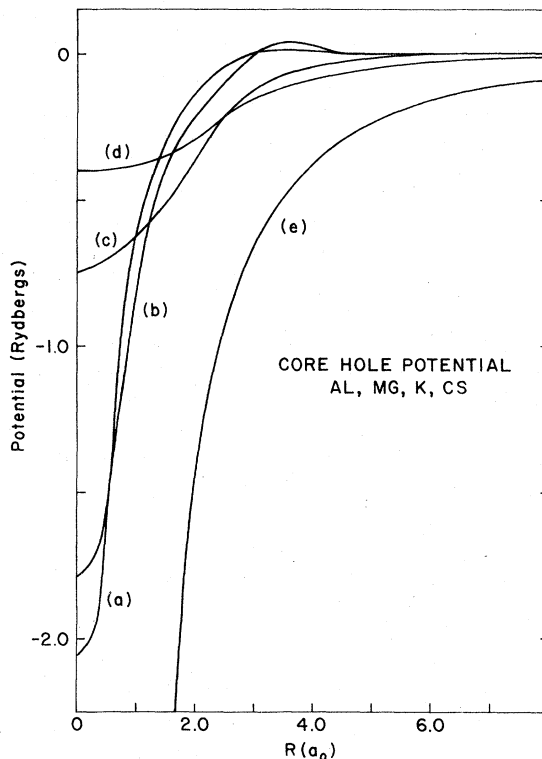


FIG. 4. Screened core hole potentials for: (a) Al, (b) Mg, (c) K, (d) Cs, and (e) $-l(l+1)/r^2$ for a d electron. The results for Mg and Al are taken from I. The screened core hole potential of Rb lies between those of K and Cs and is not shown.

than for the heavy alkali metals since the short range part of the core hole perturbation is more attractive for Al and Mg than for the heavy alkalis. This results from the structure of the core hole. The core hole is not a point charge localized at the origin. Rather, it is more realistic to treat it as a sphere of charge with much of the charge located near the edge of the sphere. This sphere would be largest in Cs and smallest in Al. The potential at the center of such a charge distribution is finite and weakest for the largest sphere. This type of structure is evident in Fig. 4.

Although the phase differences at large k for Mg are slightly larger than those for Al, this most likely occurs because we have not determined the differences at sufficiently large k to probe the region where the core hole potential of Al is more attractive than that of Mg. Similarly, the d -phase shift differences of Al and Mg are much smaller than those of the alkalis. The core hole perturbations in Al and Mg have sufficiently short range that even higher k are necessary to test the short-range behavior when the centrifugal barrier is present.

The small k differences should be sensitive to the core hole potential at large distances. At these distances the core hole potential is determined mainly by the screening. As indicated in Fig. 4, Cs has the most attractive core hole perturbation at large distances because it has the least screening. The core hole potential in Al is less attractive at large distances because the screening is more effective. One would expect that the phase differences at small k to be larger in those metals with less screening. This trend is evident for Al, Mg, K, and Rb. However, for Cs the small k phase differences are smaller than those of K or Rb even though Cs has the least screening and the potential with the longest range. There are two possible reasons for this. First, the core hole in Cs has the largest spatial extent. As a result, the core hole potential of Cs is the least attractive one at short range. It may be sufficiently weak that the lack of screening at large distances is not enough to enhance the scattering. Certainly, in the limit that the core hole had infinite extent, we would expect the s -phase shift differences to be negligible regardless of the amount of screening. The core hole of Cs may be sufficiently large that the screening contribution is no longer dominant at even small k and, as a result, the s -phase difference would be smaller. In addition, we must remember that the electron states and thus the phase shifts are determined self-consistently. Thus the phase shifts at the Fermi level must satisfy the Friedel sum rule. The core hole in Cs has such a large extent and there is so little screening that the core hole potential is not negligible compared to the centrifugal potential. Thus for Cs the d -phase differences at the Fermi level are larger than those of the other metals. Since the d phase shift is more effective at exhausting the Friedel sum, a small increase in it leads to a larger suppression of the s -phase differences.

As has been shown⁸ the phase shifts η_l needed to evaluate the x-ray edge exponents are the differences between phase shifts for electrons in systems with and without a core hole. These are the phase shift differences shown in Fig. 3. Using

TABLE VI. The threshold exponents α , α_0 , α_1 , and α_2 for (a) this work and (b) the experimental results of Ishii (Ref. 15).

	(a)				(b)
	α	α_0	α_1	α_2	α_0
K	0.12	0.28	0.04	-0.08	0.23
Rb	0.12	0.29	0.03	-0.08	0.19
Cs	0.09	0.23	0.004	0.01	0.06

these differences and Eqs. (2) and (3) we can calculate the exponents. They are shown in Table VI. As far as we know, this is the only calculation which treats each of these metals as something more than an electron gas (where only screening effects are important). Unfortunately the only available experimental results are those of Ishii for α_0 . We know of no measurements done for the heavy alkalis to determine α or α_1 .

Ishii found that α_0 decreases monotonically for the sequence K, Rb, and Cs. For K α_0 is 0.23, for Rb α_0 is 0.19, and for Cs α_0 is 0.06. We determined that α_0 is 0.28 for K, 0.29 for Rb, and 0.23 for Cs. The calculated exponents are all larger than the experimentally determined ones. Moreover the exponent for Rb is slightly larger than that of K. The difference is small and, within the accuracy of this type of calculation, not significant. However there is a significant decrease in α_0 between Rb and Cs. Again this decrease is not as large as the experimental one.

There are several possible reasons why our results differ from Ishii's. For Na, Mg, and Al the single particle spectra near threshold for transitions to d states have the same values or are smaller than the single particle spectra for s final states (see Table VII). Since α_2 is generally negative the contributions from the d spectra are ignored in the data analysis. Although Ishii followed this procedure, it may not be adequate for the heavy alkalis as our absorption cross sections show. Near threshold the d cross sections of the heavy alkalis are either the same or much larger than the s cross sections depending on the approximation we use. Moreover the d cross sections increase rapidly near threshold while the s cross sections decrease slowly from threshold. These effects should make the measured α_0 too small.

Our model may also be at fault. We overestimate the s -scattering when Na has a core hole.⁹ We may do the same for the heavier alkalis. Replacing the uniform background by a more realistic background with localized centers of attraction

TABLE VII. Ratio of s -wave to d -wave cross section at threshold: (a) for free ions using the excited-state approximation and for metals using (b) the excited-state approximation and (c) the ground-state approximation.

	(a)	(b)	(c)
Na	0.05	3.58	6.35
Mg	0.04	1.63	2.03
Al	0.03	0.69	0.92
K	2.15	0.31	1.64
Rb	0.31	0.38	1.64
Cs	0.48	0.11	0.66

would lessen the importance of the central perturbation. This correction should be more important for the heavy alkalis which have the lower charge densities. For these metals there is little screening and the error made in replacing a lattice of positive ions by a uniform background should be the largest.

The calculated exponents also disagree with those obtained from the empirical rule of Dow and Sonntag. The rule predicts that α_0 is 0.33 for K, 0.36 for Rb, and 0.38 for Cs. The differences between our results and the empirical rule are much more than the difference of 0.01 between our results for Al and Mg and the empirical rule.³⁹ Our disagreement with the empirical rule is significant in light of the results of Ishii that the α_0 are too small to agree with the rule and they decrease for K, Rb, and Cs. The empirical rule was determined by making a fit to the experimental results for Na, Mg, and Al. The phase differences used to determine the α_0 are those at the Fermi level (the wave vector is $0.72a_0^{-1}$ for Mg and $0.93a_0^{-1}$ for Al). We can see in Fig. 3 that these occur in a region where the effect of screening is more important for the phase differences of Mg and Al because the phase shift differences for Mg are larger than those for Al. This fact plus the fact that phase differences at a smaller k are used to determine the α_0 for Mg mean that the α_0 for Mg is bigger than the α_0 for Al. For K and Rb the phase differences which determine the exponents are those at $0.4a_0^{-1}$ and $0.36a_0^{-1}$, respectively. These occur in a region where the phase differences for Rb are smaller than those for K. Therefore the exponents are determined from phase differences which are more sensitive to the core hole structure. The only reason that the α_0 for Rb is the same as the α_0 for K is that it is determined using phase differences at a smaller k . The effect of the core hole structure is even more evident in Cs. The s -phase differences used to determine α_0 for Cs are smaller than those in K or Rb even though they are the phase differences at $0.33a_0^{-1}$ rather than $0.36a_0^{-1}$ or $0.40a_0^{-1}$. We should not expect the exponents of K, Rb, and Cs to fit an empirical rule which was determined from exponents more sensitive to the screening effects. Moreover the exponents we calculate should be smaller than those extrapolated from the empirical rule since including the core hole structure weakens the s scattering for metals with large core holes. This effect of the core hole structure can also be seen in several theoretical calculations^{4,6} which do not include the effect of the core hole structure and predict that α_0 should be nearly 0.5 for K, Rb, and Cs. Moreover, by including the effects of the core hole structure Longe⁴ calculated an

α_0 for Na which was twenty percent less than the α_0 he calculated using a screened point charge.

If the core hole structure can have such a large effect on the α_0 one should wonder why it does not have a larger effect on the α measured in x-ray photoelectron spectroscopy (XPS) for Na, Mg, and Al,^{40,41} for the $1s$, $2s$, and $2p$ levels. The results of Citrin⁴¹ indicate that the α for $2s$ levels are slightly larger than the α for $2p$ levels. The observed differences may not be statistically significant; however, they are the effect that the core hole structure would have. The difference between the α for the $1s$ and $2p$ levels of Mg is even larger. Although Citrin attributes this to the effect of surface contamination, it could also result from the differences in core hole structure. The main reason that there is little difference is that $2s$ and $2p$ levels have similar spherically averaged charge distributions so the core hole potentials are very similar. Moreover these levels have about the same extent and it is much less than that of the $3p$, $4p$, or $5p$ levels. As indicated in Fig. 3, there is little difference between the phase differences for $2p$ holes in Mg and Al for k near the Fermi wave vectors of these metals. Thus we expect large discrepancies in the phase differences of $1s$, $2s$, and $2p$ holes to occur only for much higher k which could probe the short range differences in different core hole potentials. Finally, the centrifugal barrier should be strong enough that differences in the $2s$ and $2p$ holes have little effect on p or higher l channels. Since the phase shifts are expected to be the same, the α should be the same. Because the phase differences of K, Rb, and Cs are most sensitive to the core hole structure at the wave vectors used to determine α and α_0 , it would be useful to have XPS measurements done on K, Rb, and Cs for core levels with the same l but different radial quantum numbers. The radial wave functions of these levels would be orthogonal so that the core holes would have different structure and different ranges. Moreover they would have sufficient size that the differences might not be negligible compared to the centrifugal barrier. One would expect to see differences in the measured α for different core levels of these metals.

We have calculated the absorption cross section for K in both the ground state and excited state approximations as shown in Fig. 5. Similar results were found for Rb and Cs. The same trends are apparent as in the free ion calculations. The cross section is rapidly varying near threshold and sharply peaked less than 10 eV from the edge. Moreover there is a maximum in the d cross section 40 eV above threshold and a second maximum 80 eV above threshold. Ishii's results for the ab-

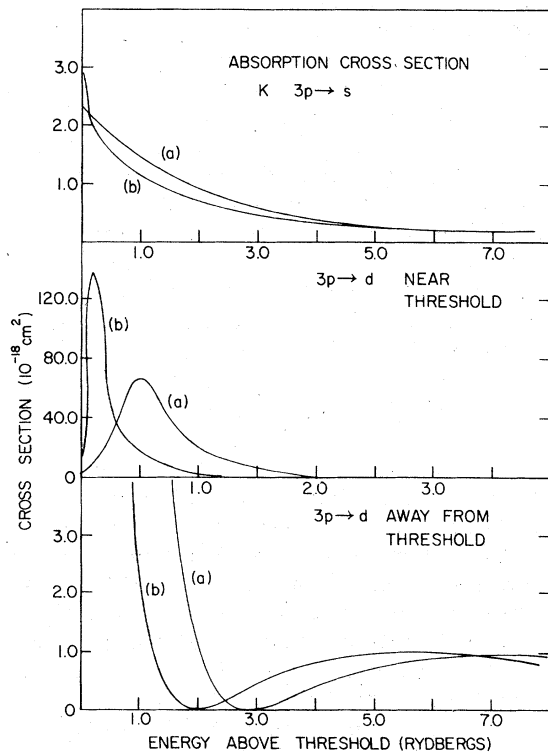


FIG. 5. Absorption cross section for K; (a) the ground-state approximation and (b) the excited-state approximation. Note the change in scale for the cross section near threshold.

sorption spectra away from threshold^{42,43} show a large peak about 8 eV above threshold and a flat spectrum starting about 15 eV from threshold. In shape this is similar to our calculation using the ground-state approximation. The magnitude of our theoretical curve calculated using the ground state approximation agrees near threshold with the experimental results. However at the peak our calculated value is much too high. This is similar to the discrepancy we found for free Ar ions. In our calculations in I the excited state approximation was better near threshold and the other was better far from threshold. For the heavy alkali metals neither approximation is obviously better because we have ignored correlation effects that are important near threshold.

We have also calculated emission cross sections assuming that the valence electron is described either by a ground-state wave function or by an excited state wave function. These are shown in Fig. 6 for K along with the experimental curve of Norris. Again, the results for Rb and Cs are similar to those for K. However no experimental results for Rb and Cs are available for comparison. In Fig. 6 the experimental emission curve for K has been scaled arbitrarily relative to each theo-

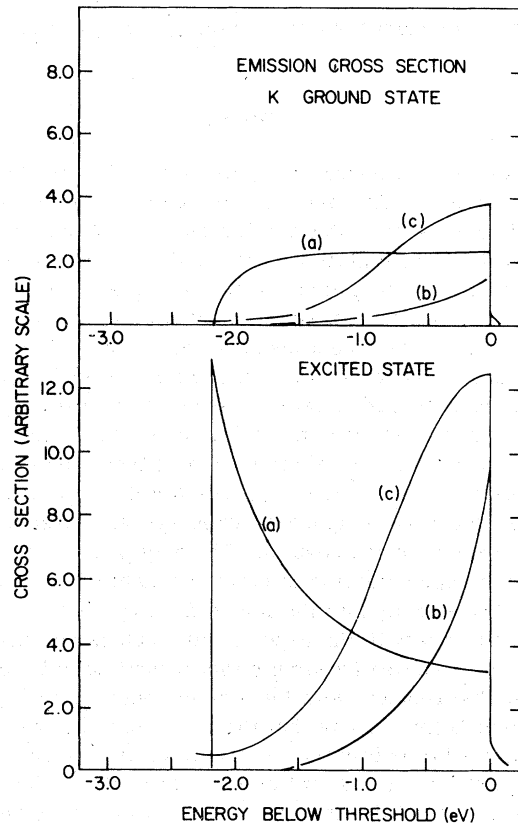


FIG. 6. Emission cross sections for K using the ground state and excited state approximations; (a) $s \rightarrow 3p$, (b) $d \rightarrow 3p$, and (c) the experimental data of Norris scaled to have the same value at threshold as the $s \rightarrow 3p$ plus $d \rightarrow 3p$ calculation. By cross section we mean intensity divided by photon frequency cubed [$I(\omega)/\omega^3$].

retical curve and the theoretical curves have been scaled relative to each other. In the excited state approximation there is a low-energy resonance not seen in experiments. This was also seen in similar calculations for Na, Mg, and Al. In the ground state approximation the resonance disappears and we see the free-electron behavior. Our cross section still does not correspond closely to the experimental curve. The low-energy region must be broadened to include the Auger tail.⁴⁴ This improves the agreement. In addition, if we scale the experimental curve in the top half of Fig. 6 to higher values, the disagreement at low energies is less. The discrepancy at higher energies could be eliminated by using the excited state approximation there. The spectrum would be described by the ground state approximation at low energies and by the other at high energies. It is known that the ground state approximation is adequate at low energies. The question remains where

and if the changeover to the other limit should occur.

IV. SUMMARY

We have extended the application of the model of I to study K, Rb, and Cs. For each metal we find self-consistent solutions for the core hole state and the ground state and calculate a threshold energy in excellent agreement with experiments. Our calculated absorption cross sections are probably not correct because we ignore important correlations in the wave functions. As in I we find that each of our emission curves in the excited state approximation has a low-energy resonance not characteristic of the observed free electron behavior. Our emission curve for K calculated in the ground state approximation agrees better with the experimental results. The question remains which approximation is better at higher energies.

We also calculate the x-ray edge exponents. Our α_0 disagree with the experimental values and with those predicted by simple theoretical calculations. The discrepancy with the experimental values may result from the way that the x-ray spectra were analyzed to obtain the exponents or it may result in part from the simplicity of our model. The discrepancy with the theoretical calculations results from the assumption that the structure of the core hole is unimportant and that only the change in screening in different metals affects α_0 .

We find that including the effects of the core hole structure lowers α_0 for metals with large core holes. It actually competes with the effect of screening. This can explain the "anomalous" decrease of α_0 with γ_s for K, Rb, and Cs. It would be interesting if the XPS index α was measured for core levels with significant differences in structure in these alkali metals. In the heavy alkalis different p levels might give different α . This would be a crucial test of the importance of the core hole structure in determining phase shifts and exponents.

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²¹The coefficient has the form

$$C_{l\pm 1} = \frac{16\pi q^2}{\hbar^2 c} \left(\frac{m}{2}\right)^{1/2} \sum_{m_l} a_{l\pm 1}^{m_l}.$$

q is the electron charge, m the electron mass, and c the velocity of light. The sum extends over the m_l with absolute value less than l or $l \pm 1$ and (Y_{lm} is the spherical harmonic function)

$$a_{l\pm 1, l}^m = \left| \int d\Omega Y_{l\pm 1, m}^*(\theta, \phi) \cos\theta Y_{l, m}(\theta, \phi) \right|^2.$$

When the energies in Eq. (7) are measured in rydbergs and the lengths in Bohr units $C_2 = 3.42 \times 10^{-18} \text{ cm}^2$, $C_0 = 1.71 \times 10^{-18} \text{ cm}^2$.

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