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Ab initio study of the x-ray edge in alkali metals and alloys

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An *ab initio* model is developed for calculating the approximate electronic structure of local excited states in alkali metals and alloys. Core excitations of Na and K metals are calculated along with core impurity excitations of K in Li and Rb in Li. Unrestricted Hartree-Fock method is used in conjunction with pseudopotentials, cluster theory, and Rayleigh-Schrödinger many-body perturbation theory to yield a spectroscopic accuracy of 0.1 eV when compared to experiment. Local resonance states below the interband threshold are found in the $(n-1)p^5s^2$ excited configurations in Na and K metals. Similar states are not found for the analogous excited configurations in dilute alloys of K in Li and Rb in Li. These results suggest that electron-hole pair interactions dominate the x-ray absorption process in pure alkali metals. Results are contrasted with current models for the enhancement of x-ray absorption.

I. INTRODUCTION

Recent experimental data on the x-ray edge in alkali-metal alloys has renewed the controversy over what effects dominate the threshold spectra in simple metals. It is observed that the shape of the threshold spectra changes as a function of isovalent impurity concentration,[1] and the controversy centers on the interpretation of these trends. Specifically, low concentrations of alkali-metal impurities in an alkali-metal host produce rounded edges in the excitation profile. Though practitioners of MND (Mahan, Nozières, and De Dominicis)[2] theory find alloys beyond the scope of their model,[3] the above trends seem to contradict MND theory since this model depends solely on the response of the host conduction electrons to the core hole. In an attempt to explain the observed experimental trends, Chiu *et al.*[1] have produced a model which is based in part on the $Z+1$ approximation. They find a qualitative agreement with experiment even though the model does not account for the dynamic response of the conduction electrons in the presence of a core hole.

Almost 20 years ago Mahan observed that exciton effects could alter the one-electron picture of the x-ray-absorption and -emission edge. He went to predict a power-law dependence of absorption near threshold that was improved by Nozières and De Dominicis. Using a noninteracting electron gas subject to a sudden change in potential, they derived the threshold behavior to have the form

$$\mu(\omega)=[\xi/(\omega-\omega_T)]^{\alpha_l}f(\omega)\Theta(\omega-\omega_T) . \tag{1}$$

Here ξ is a typical bandwidth, ω_T is the threshold frequency, and $f(\omega)$ is a slowly varying function of ω, and $\Theta(\omega-\omega_T)$ is the step function. We also have

$$\alpha_l=\frac{2\delta_l}{\pi}-2\sum_{l'}(2l'+1)\left[\frac{\delta_{l'}}{\pi}\right]^2 , \tag{2}$$

where l is the angular momentum, and δ_l is the scattering phase shift of conduction electrons in response to the core hole. Theoretical values for α_l have been calculated for a variety of metals, and fits to experimental data agree with theory after being scaled to sum rules. For systems where excitonic effects dominate the transition process, spectral line shapes have been qualitatively predicted.[3]

However, it is difficult to explain the recent experimental results of Chiu *et al.*[1] using the MND model. It seems unlikely that the response of the conduction band would be fundamentally different for an alkali atom with a core hole in a like host or as an isovalent impurity. This led Chiu *et al.* to offer an alternative explanation for the source of the x-ray-edge anomaly. Their analysis was based in part on the $Z+1$ approximation, which we will briefly review.

The $Z+1$ approximation is based on the assumption that the lowest-energy core excited state of an atom is chemically similar to its right-hand neighbor in the Periodic Table. For example, it is assumed that $\mathrm{Na}(2p^53s^2)$ and $\mathrm{Mg}(2p^63s^2)$ have a similar $3s^2$ valence structure. This approximation can be used to predict energy levels in the bulk by removing from the host lattice one atom (Na) and replacing it by its $Z+1$ neighbor (Mg). Energy levels are predicted by adjusting the atomic excitation energy of the atom by the cohesive energies of the atom and its $Z+1$ neighbor, the energy of solution, and the energy associated with relaxing the lattice around the excited state. This procedure has been successfully applied to a variety of metallic systems, including the alkali, noble, and transition metals.[4]

The purpose of this investigation is to calculate the approximate electronic structure of the excited state in several metals and alloys. These results will then be related to experiment, the $Z+1$ approximation, and MND theory. Both MND theory and the $Z+1$ approximation predict a resonance or bound state at or below the interband threshold for alkali metals. Where the models differ is in their interpretation of the source of divergence in the excitation threshold. MND theory predicts an enhanced absorption in excess of one-electron theory due to the interaction of the forming core hole with the electrons at the Fermi edge. The core hole attracts a screening cloud of electrons from states near E_F and this interaction increases the number of correct symmetry states that the excited electron can occupy. The final state of this system consists of a core hole screened by the conduction-band electrons which exhibit a characteristic phase shift. Alternately, Chiu *et al.*[1] have argued, using the $Z+1$ approximation, that the sharp excitation threshold is due to a local atomiclike excitation occurring within the bulk. Atomic transitions occurring locally and forming an electron-hole pair condensing at or below the band bottom would produce white lines in the absorption spectra. Using the $Z+1$ approximation they go on to show that in dilute alkali alloys the ns^2 levels are degenerate with the host conduction band. These nonlocal states produce a rounded excitation edge. In order to gain some insight into this problem we develop here a general many-body theory for the local photoexcitation of electrons in a metal coupled to the conduction-band electrons within the framework of a cluster model.

An accurate model for these excitations must allow for core relaxation and two-particle interactions throughout the conduction band. We accomplish this by implementing unrestricted Hartree-Fock theory augmented with correlation corrections using a size-consistent approach. This approach is more satisfying than self-consistent methods which use a rigid potential, be it a pseudopotential or a static delocalized electron orbital. Such models do not allow for the interaction of open-shell impurity-atom electrons with the hole in the excited state. The dynamic interaction of the hole with the conduction band is of paramount importance; any relaxation of the hole in the excited state must be included in such an interaction. The importance of using the final-state picture of the absorption process has been noted in the literature.[5] We intentionally do not use the orthogonalized–final-state (OFS) rules in these calculations. OFS rules are useful away from the Fermi edge, but underestimate excitonic enhancement near the Fermi edge.[6] The model developed here circumvents the fundamental difficulties encountered when running a band-structure calculation with a deep core hole.

To form the excited-state wave function we remove a one-electron eigenfunction from the ground-state occupied space and occupy a one-electron eigenfunction in the unoccupied space. In this case the two one-electron wave functions were chosen to satisfy the dipole selection rules. Therefore, by symmetry the ground- and excited-state eigenfunctions are orthogonal. Further, if we assume that there is no relaxation of the other occupied eigenfunctions in the excited state, then the ground- and excited-state determinantal wave functions are orthogonal. The oscillator strength is then proportional to the matrix element of the one-electron eigenfunctions between the dipole operator. In this study the latter approximation is invalid for the following reasons. First, in some of the excitations that we will consider, there is a substantial relaxation of the electrons not directly involved in the transition. This introduces a finite uncertainty as to which electron in the conduction band is the excited electron, and makes the simple one-electron picture of the oscillator strength inappropriate. Second, in the MND description of the x-ray-absorption process it is precisely the response of the passive electrons that produces, or quenches, the x-ray edge. Therefore, including the relaxation of the passive electrons in the presence of the core hole is a fundamental requirement when calculating the oscillator strength for these excitations.

In fact, though the general formalism to calculate oscillator strengths from nonorthogonal wave functions has been developed,[7] few workers attempt such calculations. This is due in part to the poor results obtained from such calculations using uncorrelated wave functions.[8] In the present calculations we do not actually construct the correlated wave functions. We avoid calculating the oscillator strength by considering the qualitative response of the conduction electrons to the core hole in the excited state in terms of phase shifts. Phase shifts are central to the MND picture and have been used extensively to infer the qualitative line shapes of x-ray-emission and -absorption spectra. We are interested in how the shifts differ for x-ray absorption in pure alkali metals and dilute alkali alloys, and if these phase shifts are consistent with experiment.

These studies are made possible by the use of state-of-the-art computer programs and computer systems. The programs are based on the unrestricted–Hartree-Fock (UHF) cluster method augmented with Bachelet-Hamann-Schlüter (BHS) pseudopotentials,[9,10] and extended by explicit calculation of correlation corrections by means of many-body perturbation theory (MBPT). These programs are implemented on a Floating Point System FPS-164-MAX scientific computer operating through a Digital Equipment Corporation VAX11750 computer at Michigan Technological University's recently formed Center for Experimental Computation. The programs are designed to take advantage of the parallel-pipelined architecture, which is enhanced by the addition of a set of vector-processor boards to increase the speed of computation.

II. METHODS AND COMPUTATIONAL DETAILS

Consider the normal nonrelativistic Hamiltonian

$$H=-\sum_{i=1}^{n}\frac{\hbar^2}{2m}\nabla_i^2-\sum_{i=1}^{n}\sum_{I=1}^{N}\frac{e^2 Z_I}{|r_i-R_I|}+\frac{1}{2}\sum_{i,j=1}^{n}\frac{e^2}{|r_i-r_j|}+\frac{1}{2}\sum_{I,J=1}^{N}\frac{Z_I Z_J e^2}{|R_I-R_J|}\ . \tag{3}$$

We use lower-case letters to designate electronic properties and upper-case letters for nuclear properties. The ith electron has coordinate r_i (x_i including spin), mass m, and charge e. The Ith nucleus has atomic number Z_I and position R_I. It is assumed that the nuclei are infinitely massive; the Born-Oppenheimer and Franck-Condon approximations are used as needed. In principle, one must solve the n-electron Schrödinger equation

$$H\psi_\alpha(x_1,\ldots,x_n)=E_\alpha\psi_\alpha(x_1,\ldots,x_n)\ . \tag{4}$$

Exact solutions to (4) are impractical for systems with large numbers of electrons. We choose instead to resort to a set of systematic approximations, the lowest order of which is the unrestricted–Hartree-Fock (UHF) approximation. One assumes that the many-particle wave function ψ may be written as

$$\psi_\alpha(x_1,\ldots,x_n)\approx(n!)^{-1/2}\det|\phi_i^\alpha(x_i)| . \tag{5}$$

That is, the solution is approximated by a single Slater determinant of one-electron orbitals, ϕ_i^α. In the UHF approximation these orbitals are constrained to be orthonormal and eigenstates of the z component of spin. They are not constrained to be doubly occupied nor to satisfy precise symmetry restriction. If the orbitals ϕ_i^α are chosen variationally, the Hartree-Fock equation determines the orbitals:

$$F(\rho_i^\alpha)\phi_i^\alpha=\varepsilon_i^\alpha\phi_i^\alpha , \tag{6}$$

where the density matrix ρ, is defined by

$$\rho^\alpha(x,x')=\sum_{i=1}^{n}\phi_i^\alpha(x)\phi_i^{\alpha\dagger}(x') , \tag{7}$$

and

$$F(\rho^\alpha)=-\frac{\hbar^2}{2m}\nabla^2-\sum_I\frac{e^2Z_I}{|r-R_I'|}+e^2\int\frac{\rho^\alpha(x',x')}{|r-r'|}-\frac{e^2\rho^\alpha(x,x')}{|r-r'|}P(x',x) . \tag{8}$$

In Eq. (6), $P(x',x)$ is the operator which replaces coordinate x by x'.

The resulting approximation is known as the unrestricted Hartree-Fock approximation and has been used to perform numerous practical calculations for atoms, molecules, solids, and surfaces with a high degree of success.[11,12] The electronic energy becomes

$$E=\sum_i\varepsilon_i-\int\left[\frac{1}{2}\sum_i\sum_j{}'|\phi_i^\alpha(\mathbf{x}')|^2\int\frac{|\phi_j^\alpha(\mathbf{x}')|^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}'-\frac{1}{2}\sum_i\sum_j{}'\phi_i^{\alpha\dagger}(\mathbf{x})\phi_j^\alpha(\mathbf{x})\times\int\frac{\phi_j^{\alpha\dagger}(\mathbf{x}')\phi_i^\alpha(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}'\right]d\mathbf{x} . \tag{9}$$

Using the UHF system of equations it is necessary to limit our summation over electrons and nuclear centers to a finite number. The response of a solid to some local process can be accurately modeled using a finite cluster of atoms if the process is contained within the cluster boundaries. Formally, it is useful to take advantage of the arbitrariness of the UHF equation to rotate from solid spanning Bloch-like orbitals to solutions localized within the cluster. The existence of such a rotated solution has been demonstrated by Kunz and Klein.[13]

Correct representation of the crystalline environment is a central problem when using clusters of atoms to simulate bulk materials. Proper boundary conditions will provide the correct environment for a metal. Free space boundary conditions are appropriate for metals which are by definition locally charge neutral. Another main feature of the environment is to act as a source or sink of propagating electrons. Electrons are donated or absorbed by the environment in such a way as to keep the Fermi energy constant. In this work we impose free space boundary conditions on the cluster to satisfy local charge neutrality and constrain the Fermi energy to be a constant. We will return to this latter point in Sec. III. This model has been used successfully by a variety of investigators to simulate bulk materials. For example, clusters of Zn and Cu atoms have been shown to duplicate bulk properties to within 0.2 eV at modest cluster sizes (6–13 atoms).[14]

In order to reduce the number of parameters needed to describe the electronic structure of the system, we have employed norm-conserving pseudopotentials. Norm-conserving pseudopotentials have been shown to yield accurate pseudo-wave-functions in the Hartree-Fock approximation.[9] These pseudopotentials ensure the accurate representation of the charge density of the conduction-band electrons while reducing the computational effort.

The UHF method omits correlation effects. This deficiency is corrected here using Rayleigh-Schrödinger many-body perturbation theory (RS-MBPT); perturbation is an obvious candidate for this problem, given the small corrections and the fact that the perturbing Hamiltonian is well defined (i.e., the nonaverage part of the electron-electron interactions). Correlation methods for extended systems are constrained by size-consistency considerations. RS-MBPT, on the other hand, has been shown to be size-consistent order by order to all orders in the perturbing potential.[15] The correlation model and how it applies to these systems has been developed elsewhere and is not the main thrust of this paper.[16] The result is shown below though the general formalism will not be worked out here:

$$E_2=\sum_{\substack{i,j\text{ occupied}\\ a,b\text{ virtual}\\ (i>j)\\ (a>b)}}\frac{(g_{ijab}-g_{ijba})^2}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b} , \tag{10}$$

where the ε_x are eigenvalues, $g_{ijab}=\langle ij|H_1|ab\rangle$, and E_2 is the second-order energy correction to Eq. (9). Virtual orbitals are, by definition, unoccupied states and typically have positive eigenvalues. In principle, there is a complete set of one-electron orbitals from which to construct E_2. In practice, a finite basis set of m functions is used. If we have n occupied states, E_2 becomes

$$E_2=\frac{1}{4}\sum_{i=1}^{n}\sum_{\substack{j=1\\ (j\neq i)}}^{n}\sum_{a=n+1}^{m}\sum_{\substack{b=n+1\\ (b\neq a)}}^{m}\frac{g_{ijab}-g_{ijba}}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b} . \tag{11}$$

Truncation of the virtual space is a good approximation if the virtual space is carefully selected. Bartlett and co-workers have shown that, given the proper virtual space, typically 90% of the correlation energy contained in a given basis set can be recovered using this technique.[17] For most observables only the differential correlation is important. Beck and Nicolaides[18] have devised a prescription for constructing virtual orbitals that will produce the maximum amount of correlation correction for a pair of occupied orbitals. This method has been used extensively in atomic physics and has been implemented here for the first time in a study of bulk materials. Also, the UHF equations are solved to self-consistency for every configuration in question (unless otherwise noted). Electronic relaxation effects and the electron-hole interaction are included explicitly. The photoexcitation energy is calculated by taking the energy difference of two many-electron configurations.

III. RESULTS

We considered the two alkali metals, Na and K. Four electronic configurations were calculated for each metal. For metallic clusters, the degree to which properties achieve size independence depends strongly on the property under consideration. Properties which require information from the entire cluster may change dramatically with cluster size. On the other hand, the electron density near the central cell is quite insensitive to the size of the cluster. For clusters of approximately 15 atoms the energy shifts due to cluster size are within the intrinsic error of the Hartree-Fock–MBPT method (0.1 eV).[19] For the approximation to be valid the cluster must be large enough so that the charge density in the region of interest (center of cluster) approximates the charge density at any arbitrary point in the bulk of an extended solid. Also, the spatial extent of the excited state must not extend beyond the boundaries of the cluster.

The alkali-metal clusters considered here consist of 15 atoms assembled in a bcc lattice using the bulk-nearest-neighbor distance. The central site is represented using a tightly contracted basis set in an attempt to keep linear dependence to a minimum. Correlation primitives are added to the central site, according to the Beck and Nicolades prescription,[18] and may have a large overlap with the atomic basis set. The other 14 sites are modeled using a polarizable basis set on a pseudopotential site. The polarization functions are determined by minimizing the *np* atomic excited-state energy. The functions are found to be relatively local in nature with $\langle r \rangle$ approximately equal to the nearest-neighbor distance.

Consider the ground-state configuration of the two metal clusters, Na and K. Our first task is to show that these clusters do indeed represent the bulk. Plotted in Fig. 1 is the electron density of the two different clusters compared to band calculations of Moruzzi, Janak, and Williams.[20] The HF electron density was taken along the [111] direction, whereas the muffin-tin electron density does not have an angular dependence. Agreement is excellent for the central cluster region with a relative error of approximately 10%. The charge density of the cluster's interstitial region replicates the charge density calculated using periodic boundary conditions. This suggests that the bulk environment has been successfully modeled by the cluster.

One criterion for the validity of the cluster model is that the physical phenomena must not be larger than the physical size of the cluster. With this in mind it should be clear that the excited-state configuration is the acid test of this scheme. The transition for Na is $2p^6 3s^1 \rightarrow 2p^5 3s^2$ and for K $3p^6 4s^1 \rightarrow 3p^5 4s^2$. For these alkali metals the excited state was found to be contained within the cluster. As an example, consider the ground- and excited-state charge-density maps for Na, shown in Figs. 2 and 3. The plots have been rotated into the plane of the $(n-1)p$ hole and show only mild perturbations of the second-nearest-neighbor (NN) charge distribution in the excited configuration.

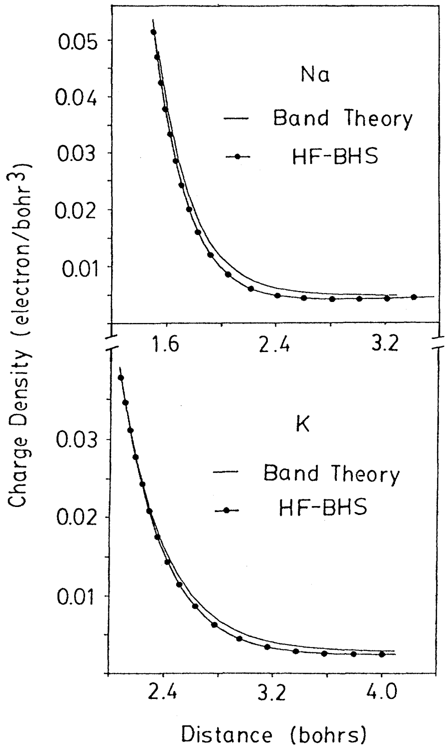

FIG. 1. Charge density in the interstitial region for Na and K metals. Solid lines represent the results of a band-theory calculation (Ref. 15) and the dotted line is from the present (SCF) cluster-model calculations.

Two other configurations were considered for each metal: the ionization of the highest-lying conduction electron and the ionization of a core electron. Total energies for each of these calculations including correlation corrections are shown in Table I. From these total energies, observable quantities are calculated. The energy differences we are interested in are shown in Table II. One-particle relativistic corrections[16] have been included for states that involve the removal of core electrons with sizable relativistic energy. The theoretical results for the photoexcitation match experimental data quite accurately and give an indication of the accuracy of our ground- and excited-state wave functions.

In a metal the conduction electrons will conspire to keep the Fermi energy constant throughout the excitation process. For a cluster in free space this may not be

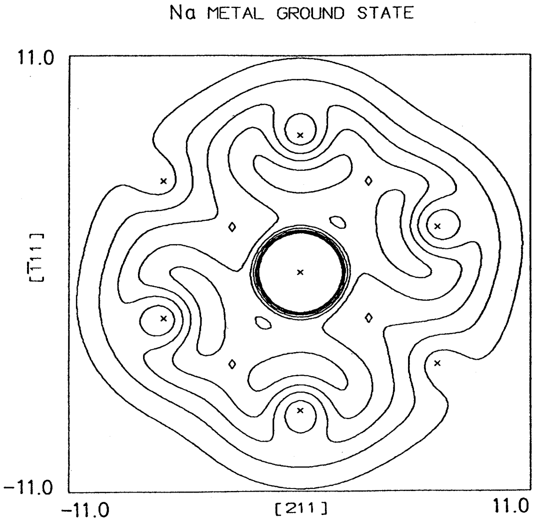

FIG. 2. Ground-state charge-density plot for Na metal. The crosses represent atoms in the plane of the contour plot. The diamonds represent atoms above and below this plane. The contour intervals are 0.01 $e/(\text{bohr})^3$.

the case. However, we expect that shifts in the top of the conduction band will approach zero monotonically with increasing cluster size. *Ab inito* calculations at this level of approximation can yield results within 0.1 eV of experiment. Therefore, cluster sizes which exhibit approximately 0.1-eV shifts in the Fermi level, in the excited configuration, are within our theoretical accuracy. Our results for Na metal indicate this degree of accuracy.

The two metals exhibit an excitonic resonance state below the interband threshold in the excited configuration. This claim may be verified by constructing

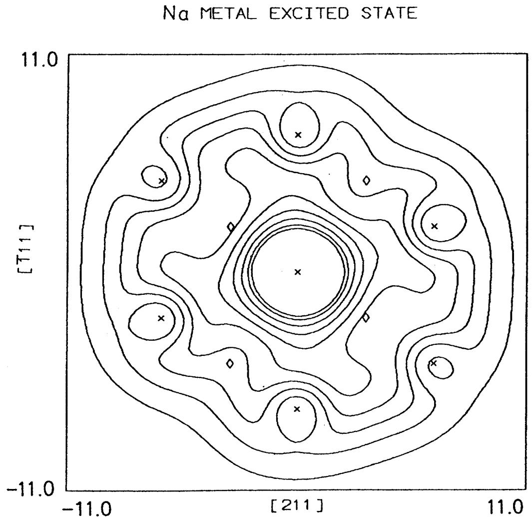

FIG. 3. Excited-state charge-density plot for Na metal. The crosses represent atoms in the plane of the contour plot. The diamonds represent atoms above and below this plane. The plot intervals are 0.01 $e/(\text{bohr})^3$.

TABLE I. Total HF-BHS energies for alkali-metal clusters; MBPT results are also included.

Metal	State	E_{HF} (H)	$E_{\text{HF}}+E_2$ (H)
Na	$2p^63s^1$	-164.5450	-164.8815
	$2p^53s^2$	-163.4904	-163.7576
	$2p^6$	-164.4436	-164.7517
	$2p^53s^1$	-163.3746	-163.6144
K	$3p^64s^1$	-600.7558	-601.0977
	$3p^53s^2$	-600.1494	-600.4181
	$3p^6$	-600.6778	-600.9916
	$3p^54s^1$	-600.0563	-600.3064

a simple picture of the conduction band using the data from Table II and the eigenvalue of the lowest-energy electron in the conduction band. We construct the band diagrams for the ground and excited states using the following procedure. The top of the band is defined as the minimum energy required to remove a conduction electron from the ground-state cluster. The band bottom is assumed to be the lowest-energy eigenvalue in the conduction band. In order to keep the Fermi energy constant the excited-state energies are shifted by the small positive energy ($E_f-E_f^*$). The conduction band and the shifted energies for the excited-state system are shown in Fig. 4. We observe a significant lowering in the band bottom in the excited configuration, 0.63 and 0.35 eV for Na and K, respectively. Assuming that the disturbance to the metal is small, the periodic symmetry of the metal excludes electrons from the band gap. Therefore, we identify the electron at the band bottom as local screening state which is formed in response to the core hole. The electron has a large effective mass and indicates the presence of a local resonance state at or below the band bottom. In order to observe the nature of this state the total charge densities of the ground and excited states were subtracted, yielding a picture of the flow of electrons in response to the excitation. For example, as shown in Fig. 5, the excitonlike screening electrons for K form a local $l=0$ state extending half the NN distance into the bulk. Na forms a similar excitonlike state in the excited configuration. These calculations are consistent with both the $Z+1$ approximation and MND theory, in that we observe the formation of a local resonance at or below the band bottom. The self-consistent-field (SCF) calculations also show a localization of an ns^2 pair of electrons around the excited atomic site. This is consistent with the $Z+1$ approximation's basic premise that the excited state of an alkali $(n-1)p^5ns^2$ looks chemically like that alkali metal's neighbor to the right in the Periodic Table. The response of the conduction electrons is also consistent with MND theory, which predicts a large positive δ_0 (scattering phase shift). This phase shift is evident in Fig. 5.

The alkali alloys are chemically similar to pure alkali metals in the free-electron model. In these calculations two dilute alkali alloys were considered, corresponding to 7% concentrations of K in Li and Rb in Li. The x-ray edge of alkali impurity atoms is almost uniformly round-

TABLE II. Experimentally measurable quantities derived using the ΔSCF method with MBPT.

Metal	Configuration Initial	Configuration Final	ΔE (eV)	Experimental energy (eV)
Na	$2s^63s^1$	$2p^53s^2$	30.66	30.68(24)
	$2p^63s^1$	$2p^6$	3.53	
	$2p^53s^2$	$2p^53s^1$	3.89	
	$2p^63s^1$	$2p^53s^1$	34.55	
K	$3p^64s^1$	$3p^54s^2$	18.65	18.5(25)
	$3p^64s^1$	$3p^6$	2.89	
	$3p^54s^2$	$3p^54s^1$	3.04	
	$3p^64s^1$	$3p^54s^1$	21.68	

ed for low impurity concentrations.[1] The two alloys K-Li and Rb-Li are no exception, as shown in the experimental data after Chui *et al.*[1] (Fig. 6). The clusters used to model these alloys were developed using the same techniques described earlier in this paper with the addition of introducing a relaxation of the host lattice around the impurity atom. This was carried out by dilating the cluster in a breathing mode and satisfying the energy-minimization principle. Movement of the impurity atom off the central site was found to be energetically unfavorable. Ground and excited states were calculated using the same procedures outlined for the alkali metals. These data are shown in Table III. The excited state is contained within the cluster in both cases and the cluster model is valid for these excitations.

Using the ΔSCF approximation we calculate observables by taking energy differences from Table III. For these excitations it is necessary to correct for one-particle relativistic effects.[21] For example, the ionization of a $4p$ electron from Rb can contribute 0.61 eV to the $4p^65s^1 \rightarrow 4p^55s^2$ excitation energy. Including these corrections, we find an excitation energy of 18.45 eV for the $3p^6s^1 \rightarrow 3p^5s^2$ transition of K and 15.04 eV for the $4p^65s^1 \rightarrow 4p^55s^2$ transition of Rb. The experimental values for these excitations are 18.5 and 15.5 eV, respectively.[1] The results are quite good, though the difference between experiment and theory for Rb in Li indicates that a better approximation of the relativistic effects may be needed.

The two alloys do not exhibit the formation of a local state at or below the band bottom. This can be seen by plotting the conduction bands for the two alloys using the procedure outlined for the alkali metals (see Fig. 7). The excited-state conduction-band bottom actually rises relative to the ground state. There is evidence that the core hole and associated screening cloud is acting as a repulsive potential to the conduction electrons. Charge-density-difference plots show that the response of the band is local but an admixture of several angular momentum states. Qualitatively, δ_0 is approximately equal to zero. The excited electron in the two alloys is degenerate with the conduction band and has even parity. We interpret this to be consistent with the prediction of Chiu

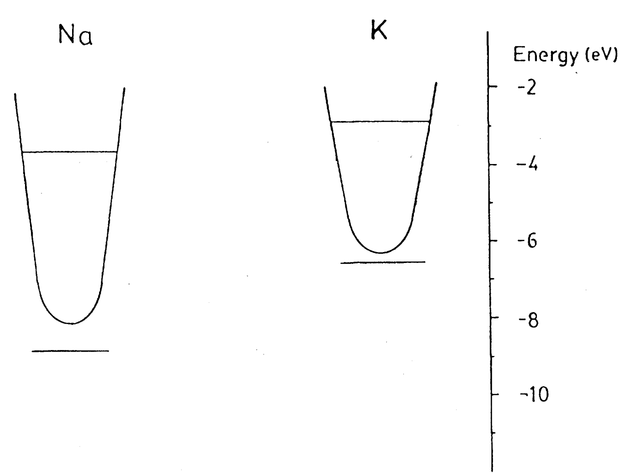

FIG. 4. Simple band diagrams for the conduction band in Na and K.

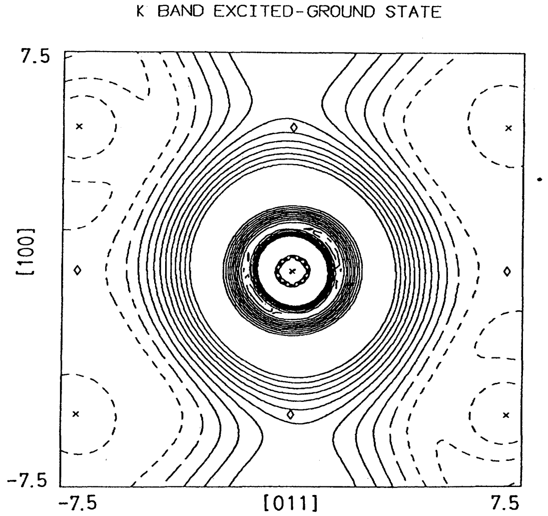

FIG. 5. Charge-density plot for the difference between the charge densities of the excited and ground states of K metal. Solid lines represent an accumulation of charge. The contour intervals are 0.002 $e/(\mathrm{bohr})^3$.

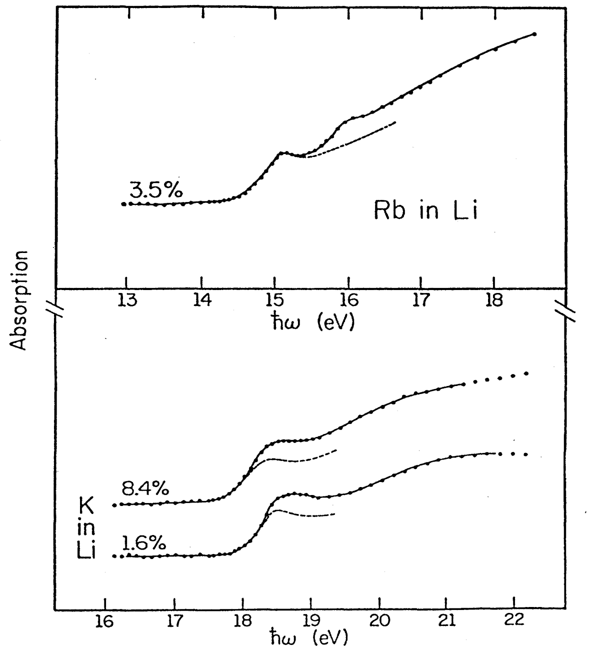

FIG. 6. X-ray-absorption spectra after Ref. 1.

et al.[1] that the ns^2 level is degenerate with the host conduction electrons.

In connection with MND theory we offer a heuristic model for the repulsive nature of the impurity atom with a core hole. This may be due in part to the Pauli exclusion principle. The host conduction electrons are orthogonal to the core states at every site in the crystal.[22] For host sites this entails producing enough local nodes to form an *ns* state. At the impurity site the host conduction electrons feel a repulsive potential because they cannot occupy the *ns* shell. In the ground state the phase shifts introduced by the impurity must sum to zero for isovalent solutes. We deduce that electrons are being scattered from *s* to higher angular momentum states. Therefore, the interaction of the impurity with the host conduction band may reduce the Mahan enhancement term for excitation to an $l=0$ symmetry state. The screening of the hole by the host conduction electrons must compete between the Coulomb attraction of the hole to the band electrons and the Pauli repulsion of the impurity core levels. A consequence of this dynamic interaction is that the hole perturbs the wave functions of a large number of the host conduction electrons and the transition probability to states near threshold is severely reduced due to the "orthogonality catastrophe."[23] Our calculations support the idea that the rounded x-ray edge for the dilute alkali alloys is due in part to Anderson suppression effects at threshold. Further trends in threshold behavior in alloys can be qualitatively explained using these ideas.

TABLE III. Total HF-BHS energies for alkali-metal alloy clusters; MBPT results are also included.

Alloy	State	$E_{\rm HF}$ (H)	$E_{\rm HF}+E_2$ (H)
K-Li	$3p^64s^1$	−601.4025	−601.6994
	$3p^54s^2$	−600.8098	−601.0244
	$3p^6$	−601.3096	−601.5837
	$3p^54s^1$	−600.6913	−600.9040
Rb-Li	$4p^65s^1$	−2938.5577	−2938.7704
	$4p^55s^2$	−2938.0599	−2938.2398
	$4p^6$	−2938.4697	−2938.6427
	$4p^55s^1$	−2938.9407	−2038.0822

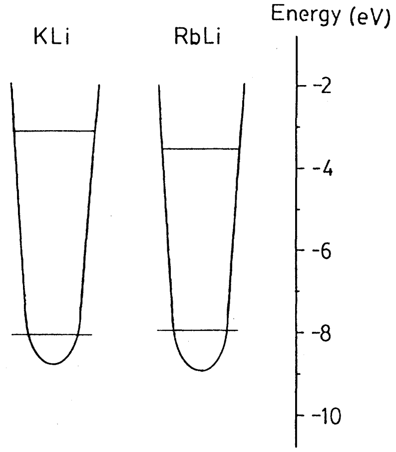

FIG. 7. Simple band diagrams for the conduction band in Li-K and Li-Rb.

Two trends are evident in considering the enhancement of x-ray absorption in alkali-metal alloys. First, for low impurity concentrations, the larger the disparity in atomic numbers of the host and impurity atoms, the more rounded the x-ray edge. Also, as the impurity concentration increases, the edge gets more pronounced. In the first case, as Z increases for the impurity atom, the ns^2 shell becomes more localized around the core hole, making screening by the host *ns* band more difficult. For the second case, as the number of impurity atoms increases, the number of electrons with quantum numbers favorable for Mahan enhancement increases. When enough conduction electrons are available to enhance absorption by forming a bound *ns* electron-$(n-1)p$ hole complex, the sharp x-ray edge emerges from the background. These observations are consistent with what has been proposed using the $Z+1$ approximation.

Our results are consistent with what has been calculated using MND theory[3] and the experimental alkali-metal alloy data. In the pure alkali metals we find that the core-hole interaction is attractive and for the most part an $l=0$ interaction. This corresponds to a large positive δ_0 for the scattered electrons in the alkali metals. For the alloys, experimental results would suggest a weakly attractive potential for $l=0$ electrons. In MND theory this corresponds to small values of δ_0, which is consistent with our calculations.

The scattering phase shifts used in MND theory cannot be calculated explicitly using this model. The finite nature of the cluster model produces a surface dipole charge imbalance in the cluster. This effect, which is small compared to the excitations outlined above, has an effect on the wave functions in the region of space where the scattering phase shifts would be evaluated. Also, even if one were to calculate these parameters, they would not match other theoretical results which implement a static core potential.

IV. CONCLUSION

The intent of this paper was to settle some of the ambiguities between the various theoretical pictures of x-ray-absorption and experimental results for some simple metals. We hoped to accomplish this by calculating the approximate electronic structure of the ground and excited states of several alkali metals and alloys using the unrestricted–Hartree-Fock method with correlation corrections. This model yields accurate spectroscopic results (within 0.1 eV of experiment) at a moderate expense of computer resources. As discussed in the text, we find evidence for the existence of local resonance states below the band bottom for excited states in Na and K metals. Similar calculations on dilute alloys of K in Li and Rb in Li show no evidence of such states. These observations are consistent with the recent experimental results of Chui *et al.*[1] The qualitative phase shifts found for these excitations are compatible with a MND interpretation of experimental results. Further, we do not find the predictive attributes of the $Z+1$ approximation, as applied by Chui *et al.*, to preclude a MND interpretation of experimental trends in the absorption threshold of alkali alloys.

Excitations for these materials have been calculated using a variety of approaches but we believe that these are the first *ab initio* calculations that verify the existence of local resonance states below the interband threshold. The one-electron approximation cannot be used to explain the absorption spectra of these excitations. This implies that electron-hole pair interactions produce the dominant effect in the near-edge x-ray-absorption spectra for these materials. These results offer a many-particle interpretation of enhanced x-ray absorption which is in agreement with the work of Mahan, Nozières and De Dominicis.[2]

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