

Spin-density calculations for core-electron photoemission and Auger electron line shapes, x-ray-edge exponents, and solid-state shifts

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Spin-polarized density-functional conduction-electron screening calculations for core ionization and Auger transition for elements Li, Be, Na, Mg, Al, and Ca are performed. The screening is described by conduction-electron scattering phase shifts obtained from self-consistent-field *ab initio* calculations. Both spins are treated separately in order to study the spin-polarization effects. The core-electron states are resolved by a Hartree-Fock-Slater method, which makes it possible to apply the same local-density exchange and correlation approximation to all electrons, including the conduction electrons. X-ray-edge exponents and x-ray photoelectron (XPS) line singularity indices are extracted from the phase shifts. Auger line singularity indices are also evaluated. In the case of Na, Mg, and Al metals the results agree with those of the previous spin-symmetric calculations and experimental values. The screening of Li and Be is, however, strongly spin-polarized, which both increases the singularity index and decreases the edge exponents. This partly explains the broad *K* edge of Li. The spin-polarized method seems to be necessary to describe the peculiar conduction-electron response to the core hole in Ca. The screening in this case is localized in energy, totally spin polarized, and of *d*-electron type. This should cause very broad x-ray edges and the most asymmetric XPS and Auger lines. By performing the corresponding free-atom calculations with the same method, the solid-state shifts (extra-atomic relaxation energies) for the photoelectron energies (binding energies) and Auger electron energies are obtained. The density-functional results agree better with the experiments than the results of the excitonic model or excited-atom model, for example. In the case of Ca the shift values are exceptionally large due to the localized *d*-electron screening.

I. INTRODUCTION

The density-functional formalism was introduced to treat inhomogeneous electron systems by Hohenberg, Kohn, and Sham.^{1,2} They proved that electron density as a basic variable determines uniquely the ground-state properties of an interacting electron gas in an external potential. By including exchange and correlation via the local-density approximation,² this formalism provides a simple method for numerical self-consistent-field (SCF) calculations, even treating the spins separately.^{3,4} The density-functional formalism has proven its applicability to many electron systems from metals to free atoms also in numerical calculations.⁴⁻⁹ It has successfully been used to describe the electron structure of impurities both in bulk metals¹⁰⁻¹² and chemisorbed on metal surfaces,¹³ or the electron structure of metal surfaces and interfaces.^{14,15} The density-functional method can be applied also in band-structure calculations.¹⁶ The wide range of applicability of this formalism makes it possible to compare solid-state, atomic, and

molecular electronic structures within the same model.

Consider an atomic—core-electron transition in a metal atom in the presence of conduction electrons, as compared to the corresponding free-atom transition. In the former case there is a conduction-electron response to the change of the atomic charge distribution and potential. This is called screening or extra-atomic relaxation, which is known to affect both the transition energies and intensities. The screening is reflected in the partial-wave scattering phase shifts of the conduction electrons in the approximation of spherical symmetry. These phase shifts yield the x-ray transition edge shape and the photoelectron line asymmetry as described by the edge exponent and the singularity index relevant to the spherically symmetric theory of Mahan, Nozières, and De Dominicis^{17,18} (MND). With the application of density-functional formalism, numerical spin-symmetric calculations on these subjects have previously been done.^{5,6} The free-atom—metal shifts or the solid-state shifts of atomic binding en-

ergies due to the screening have also been estimated by a number of methods ranging from pure atomic^{19,20} to semiempirical²¹⁻²³ and density-functional *ab initio* calculations.^{7,8} The calculations have already been extended to the case of Auger transitions.^{8,19,20,22,23}

In this paper spin-polarized density-functional (SDF) self-consistent-field calculations for Li, Be, Na, Mg, Al, and Ca are presented.²⁴ Ground states and single- and double-hole states are treated in order to obtain the changes both in the conduction-electron phase shifts and the total energies for some transitions. From these, the x-ray-edge exponents, the singularity indices relevant to the line shape, and the solid-state shifts are evaluated. In addition, the Auger line asymmetry is considered in terms of the singularity index. The effect of the spin polarization of the screening of excited states is discussed, especially in the case of metallic Ca.

The *ab initio* calculation method employed in this work is essentially the same that was previously used by Nieminen and Puska for impurity¹¹ and relaxation shift^{8,23} calculations. However, a short description of the method and calculations is first given. The spin-polarized extensions of the applied MND equations are also given.

II. METHOD OF CALCULATION

We perform the SCF-SDF *ab initio* calculations in order to find the electron structure of an atom in jellium and the electron structure of a free atom. A short description of this method is given here, but more details are found in Refs. 8 and 11. To describe the metallic environment of an atom, a jellium model with a spherical vacancy is adopted.¹⁰ This is defined by two parameters: the electron-gas density parameter r_s and the number of valence electrons per atom Z_h . The values used in this work are found in Table I. These two parameters together define the Wigner-Seitz radius R_{WS} of the spherical vacancy in the jellium by $Z_h r_s^3 = R_{WS}^3$. The nucleus of the element considered is placed at the center of the vacancy. In the potential thus created there exist bound- (core-) electron states and scattering- (conduction-) electron states occupied up to the Fermi level. All of those one-electron states are worked out self-consistently using the local-density spin-polarized exchange and correlation potential approximation of Gunnarsson and Lundqvist.⁴ A routine similar to the Hartree-Fock-Slater subroutine of Herman and Skillman²⁶ is used to resolve the bound eigenstates. This allows us to treat spins separately, i.e., to obtain the spin components of the charge

TABLE I. Free-electron density parameter r_s , number of valence electrons Z_h for the jellium vacancy model (Ref. 25), and the largest r value R_0 in the spherical position space.

	Li	Be	Na	Mg	Al	Ca
r_s (a.u.)	3.25	1.87	3.93	2.66	2.07	3.27
Z_h	1	2	1	2	3	2
R_0 (a.u.)	13	9	19	19	20	20

density. For conduction electrons the free-electron model is basically applied, and the scattering is considered as a correction to the model.

The lattice structure is not taken into account. As a correction to the jellium model a spherical average of the true lattice potential can be included.^{5,11} However, its effect upon the transition energies has been found to be negligible⁸ due to the large cancellation from taking the difference of the two total energies of two separate SCF calculations (Δ SCF method). This type of cancellation also reduces other possible errors arising from the jellium model in Δ SCF calculations. A further cancellation is obtained in taking differences of the Δ SCF values as is done in the solid-state shift evaluation. For example, the core-hole self-energy errors that are not negligible⁵ in the transition energies calculated by density-functional method are hence canceled out. The density-functional theory is rigorously valid only for a ground state of each symmetry. However, as long as the potential of a core hole can be regarded as an external potential, the theory should be applicable. In any case, there is at least empirical evidence of this,⁴⁻⁸ which can be clearly seen also from the results of this work.

The numerical computations were performed by the method of successive iterations until a satisfactory convergence was achieved. Conventional feedback or the damping method was applied to create a new potential function for a next loop. In the spherical position space the r axis was discretized into a Herman-Skillman mesh²⁶ consisting of consecutive blocks of increasing length doubling the mesh size over the preceding one, each block being divided into an equal number of subintervals. The total number of the subintervals varied from 400 to 500 depending on the element, and the length was chosen to be small compared to that of the charge-density variations near the nucleus and the wavelength π/k_F of the conduction-electron charge-density oscillations (Friedel oscillations) at larger r values. The largest r value R_0 for each element was chosen to include totally the core-electron charge

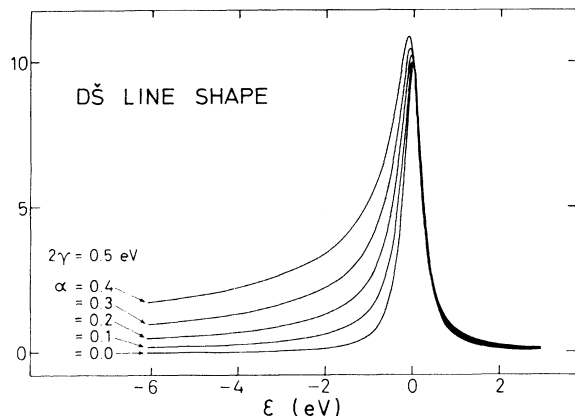


FIG. 1. Doniach-Šunjić line shape from Eq. (4) incorporating Lorentzian lifetime broadening of $2\gamma=0.5$ eV. The intensity is normalized to 10 at 0 eV for each curve, which demonstrates the shift of the point of maximum intensity. Note also the strong increase of the peak area (or the decrease of the maximum intensity) with the increase of the singularity index α .

densities and some Friedel oscillations; see Table I.

In the case of the double-hole state of Al this was not successful owing to loosely bound and diffuse 3s orbitals. A slight variation of R_0 was used to optimize the charge neutrality among the different hole states of each element. In the free-atom computations R_0 was always sufficiently large to cover the numerically calculable charge density. The maximum number of the angular momentum partial waves included was ten. The energy space discretization for the conduction electrons to not more than 100 intervals was nonlinear depending on the structure of the density of states (DOS). The NAG FORTRAN library²⁷ subroutines were employed for routine duties, such as integrations.

The spherically symmetric solution of the bound- and continuum-electron states of an embedded metal atom determines the energy-dependent partial-wave phase shifts $\delta_l(\epsilon)$ and their derivatives. These entities, the latter yielding the density of states, describe directly the conduction-electron-gas response in the energy space to the potential of the atomic nucleus, which is considered as an external potential. Change of this response due to an atomic transition, e.g., ionization, creates screening around the ion to preserve the overall charge balance. Mahan, Nozières, and De Dominicis^{17,18} theoretically predicted the band transition x-ray absorption and emission edge shape using these phase shifts. With regard to a structureless recoilless core hole with an angular momentum quantum number l , they show that the x-ray transition rate near the threshold ϵ_T asymptotically behaves as

$$I_l(\epsilon) = A_l(\epsilon) \left(\frac{\epsilon_0}{\epsilon - \epsilon_T} \right)^{\alpha_l}, \quad (1)$$

where

$$\alpha_l = \frac{2\delta_l(\epsilon_F)}{\pi} - \alpha, \quad (2)$$

$$\alpha = 2 \sum_l (2l+1) \left(\frac{\delta_l(\epsilon_F)}{\pi} \right)^2, \quad (3)$$

$A_l(\epsilon)$ is an ordinary one-body transition amplitude, and ϵ_0 is a cutoff energy of the order of Fermi energy ϵ_F . The degeneracy coefficients 2 and $2l+1$ in Eq. (3) come from (symmetric) spins and magnetic quantum numbers, respectively. The total x-ray response function is obtained from Eq. (1) by summing it over l and its degeneracy and using a step function to describe the edge. Depending on the relative magnitude of the terms in the difference (2) α_l can be either positive or negative, the first case causing sharpening and the second case rounding of the edge.^{18,28}

Doniach and Šunjić (DŠ) studied not only the x-ray-edge shape but also the effect on the kinetic energy of a core electron ejected from an atom.²⁹ The x-ray photoelectron spectroscopy (XPS) transition produces a fast photoelectron under very different transition rules. Under these circumstances the first term in Eq. (2) does not contribute, and the additional transition rate is determined only by α in Eq. (3), the singularity index. DŠ also gave a closed form to the XPS line²⁹:

$$I(\epsilon) = \frac{\Gamma(1-\alpha) \cos \left[\frac{\pi\alpha}{2} + (1-\alpha) \arctan \left(\frac{\epsilon}{\gamma} \right) \right]}{(\epsilon^2 + \gamma^2)^{(1-\alpha)/2}}, \quad (4)$$

as a convolution of the Lorentzian line with full width at half maximum (FWHM) of 2γ describing the natural lifetime broadening and the asymmetric singular energy spectrum $\epsilon^{\alpha-1}$ due to the screening. The latter can be physically interpreted to be the energy spectrum of electron-hole excitations near the Fermi level where the infinite number of infinitely small excitations are the origin of the singularity. This gives the name singularity index. The many-body line shape of Eq. (4) is demonstrated in Fig. 1 for a set of different values of α and using $2\gamma=0.5$ eV.

Because of charge neutrality the total integrated charge must vanish in a sphere of sufficiently large radius except for small decaying Friedel oscillations. In the energy space the charge-balance condition is

formulated as the Friedel sum rule³⁰

$$Z = \sum_L \frac{\delta_L(\epsilon_F)}{\pi}, \quad (5)$$

where the notation $L = (l, m_l, m_s)$ for the set of electronic quantum numbers is used and Z is the positive charge, the nucleus, to be neutralized. This form is not restricted by the spin symmetry. In our calculations no constraints have been imposed on the Friedel sum. Hence the average deviations of 0.005 for ionizations and 0.02 for Auger transitions from the exact difference value of 1 describe the quality of self-consistency and numerical accuracy. Also, Eqs. (2) and (3) can formally be extended to a spin-polarized form as follows:

$$\alpha_L = \frac{2\delta_L(\epsilon_F)}{\pi} - \alpha \quad (6)$$

and

$$\alpha = \sum_L \left[\frac{\delta_L(\epsilon_F)}{\pi} \right]^2. \quad (7)$$

where the meaning of α_L should be interpreted in terms of the LS -coupling scheme,³¹ to be discussed later.

According to MND the phase shifts should be determined from the self-consistently screened hole potential. In our model, however, the reference state

(free-electron conduction band) does not describe the initial state before creating the hole since there is conduction-electron scattering also from the initial-state atomic potential. Therefore the phase shifts relevant to the MND model are *differences* between the Fermi-level phase shifts for SCF potentials with and without the core hole in our case, as has been shown also in the Appendix of Ref. 5. These Δ SCF quantities are called transition phase shifts. According to the Friedel sum rule (5) the transition phase shifts clearly describe the screening due to the hole potential, whereas the phase shifts calculated from the difference potential, i.e., the Δ SCF hole potential, do not necessarily obey the sum rule without some additional constraints. It should be emphasized that in our model the only parameters are those given in Table I. Similarly, we may assume the relevant phase shifts for describing the conduction-electron response to the Auger transition to be the differences of the final- and initial-state phase shifts, the transition phase shifts. In the Auger transition as in the XPS transition a fast electron is ejected, and the conduction-band electrons are not explicitly involved, either. According to this analog the theory and the equations given above can be extended to include also the Auger line shape.

The solid-state shift or the screening energy (also called extra-atomic relaxation energy) is the change in the binding energy (photoelectron energy) or the

TABLE II. Singularity indices α calculated by the SDF method compared with other calculations (Refs. 5, 6, 38, and 40) and experimental values (Refs. 33–35). The spin-symmetric (-averaged) SDF values do not deviate from the spin-polarized ones and are not tabulated here (see text). The experimental errors are given in parenthesis.

Core hole	Na	α Mg	Al	Reference	
This work					
1s	0.168	0.130	0.120	SDF	
2s	0.158	0.114	0.098		
2p	0.157	0.115	0.099		
Calculated					
2p	0.20		0.13	Almbladh <i>et al.</i> (Ref. 5)	
2p	0.32 ^a	0.12	0.10	Bryant <i>et al.</i> (Ref. 6)	
	0.21	0.13	0.11	Minnhagen (Ref. 38).	
Experimental					
Average	0.19(1)	0.12(1)	0.10(1)	Steiner <i>et al.</i> (Ref. 33)	
1s	0.21(2)	0.15(2)	} Citrin <i>et al.</i> (Ref. 34)	Citrin <i>et al.</i> (Ref. 34)	
2s	0.205(15)	0.130(15)			0.12(2)
2p	0.198(15)	0.126(15)			0.118(15)
2s		0.132(12)			0.161(8)
				Ley <i>et al.</i> (Ref. 35)	

^aFrom Ref. 40.

TABLE III. Threshold exponents α_l by the SDF method and the corresponding spin-symmetric (ss) values (see text). Comparison with other calculated (Refs. 5, 6, 37, 39, 40, and 44) and experimental (Refs. 32 and 36) values. Because of the core-hole independence, only averages are given.

Na			Mg			Al			Reference
α_0	α_1	α_2	α_0	α_1	α_2	α_0	α_1	α_2	
This work									
0.28	0.01	−0.16	0.17	0.09	−0.11	0.11	0.11	−0.09	SDF
0.30	0.03	−0.16	0.18	0.10	−0.11	0.12	0.12	−0.09	SDF (ss)
Calculated									
0.38	−0.05	−0.20				0.06	0.14	−0.12	Almbladh <i>et al.</i> (Ref. 5)
0.47 ^a	−0.26 ^a	−0.31 ^a	0.19	0.10		0.13	0.12		Bryant <i>et al.</i> (Ref. 6)
0.34	−0.02	−0.12	0.25	0.06	−0.07	0.24	0.05	−0.05	Mahan (Ref. 37)
0.41	−0.11	−0.18							Longe (Ref. 44)
0.42	−0.13	−0.20							Ausman <i>et al.</i> (Ref. 39)
Experimental									
0.26(4)			0.18(4)			0.15(4)			Dow <i>et al.</i> (Ref. 36)
0.37	−0.07		0.22	0.10		0.16	0.10		Wertheim <i>et al.</i> (Ref. 32)

^aFrom Ref. 40.

Auger electron kinetic energy due to the surroundings of an atom in solid phase. Now, in addition to the metallic phase calculations, similar free-atom calculations are needed for reference. The free-atom calculations performed in this work are a limiting case of the above-described jellium calculations in the sense that r_s grows to infinity and the bandwidth goes to zero. The perfect screening process in the energy space requires one electron to be added to the Fermi level per core hole in metal. It means that the calculated kinetic energy of an ejected electron is referenced to the Fermi level. This is the case also in most of the experimental measurements. The Fermi level lies below the vacuum level by a work function Φ , which must be obtained experimentally. The natural reference level of the atomic-electron emission is the vacuum level, also due to the limiting process discussed above. If the binding-energy shift is given in the form of the kinetic energy shift of a photoelectron ΔE_{XPS} , the solid-state shifts are

$$\Delta E_{\text{XPS}} = E_B^a - E_B^s - \Phi$$

and

$$\Delta E_A = E_A^s - E_A^a - \Phi,$$

(8)

where subscripts A and B refer to the Auger electron energy and binding energy, respectively, and superscripts a and s to the free atom and solid state. These shifts so defined are both normally positive, the binding-energy shift ΔE_B being the negative of ΔE_{XPS} .

There are two possible spin combinations for each double-hole state and possibly a larger number of spin-hole configurations for free atoms due to the presence of an open valence shell. The quantum numbers of the core electrons (or holes) may be assigned to those of the LS coupling. Hence the useful concept of the configurational average³¹ is adopted. In order to find the configurational average for a hole configuration, calculations for all pos-

TABLE IV. Singularity indices α and the threshold exponents α_i for Li and Be by the SDF method compared to the other calculated (Refs. 5, 6, 37–39, and 43–45) and experimental (Refs. 33–36) values.

α	Li			α	Be			Reference
	α_0	α_1	α_2		α_0	α_1	α_2	
				This work				
0.181	0.06	−0.06	−0.20	0.132	0.04	0.06	−0.13	SDF
0.154	0.20	0.09	−0.17	0.124	0.10	0.13	−0.12	SDF (ss)
				Calculated				
0.16	0.27	0.05	−0.17					Almbladh <i>et al.</i> (Ref. 5)
0.16	0.23	0.08						Bryant <i>et al.</i> (Ref. 6)
	0.42	−0.13	−0.21					Mahan (Ref. 37)
0.24				0.13				Minnhagen (Ref. 38)
0.159	−0.16	0.04	−0.14					Girvin <i>et al.</i> (Ref. 43)
	0.39	−0.08	−0.16		0.33	−0.02	−0.09	Longe (Ref. 44)
	0.41	−0.10	−0.18					Ausman <i>et al.</i> (Ref. 39)
				0.09	0.25	0.05	−0.05	Leiro (Ref. 45)
				Experimental 0.05(1)				Steiner <i>et al.</i> (Ref. 33)
0.23(2)								Citrin <i>et al.</i> (Ref. 34)
0.18(3)								Ley <i>et al.</i> (Ref. 35)
		−0.3						Dow <i>et al.</i> (Ref. 36)

sible spin combinations were carried out. Hereafter, unless otherwise mentioned, the evaluated quantities refer to the configurational average of the possible spin combinations. A further consideration of the energy differences between the different spin configurations would give some information on the multiplet structure.⁹ Thus there exists a possibility for studying the change of this structure in going from free atoms to the metal phase.

III. RESULTS

From the experimental data the singularity indices and edge exponents may be extracted by

several methods,³² the most reliable being the fitting of the whole measured spectrum.^{33,34} A method where an asymmetry index is determined from the relation of the line position to its halfwidth is also used,³⁵ in connection with its analytical dependence on the singularity index.²⁹

The Na, Mg, and Al metals have previously been studied both theoretically and experimentally,^{5,6,32–40} and in this work they are considered as examples of spin-symmetric screening as compared to Li, Be, and Ca. The singularity indices α for the XPS lines of these metals calculated in this work are given in Table II for each core ionization separately. A comparison with some experimental and previous-

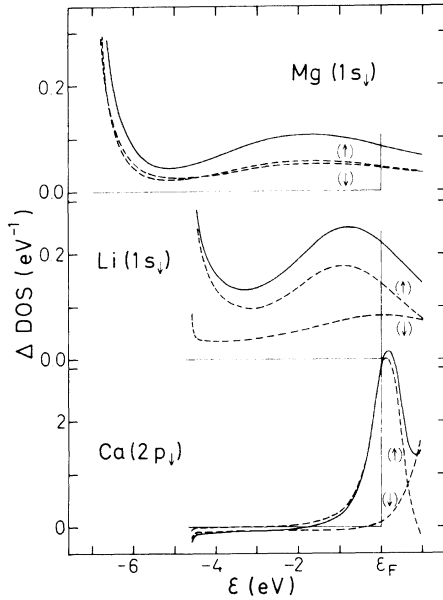


FIG. 2. Change in local density of states (ΔDOS) for metal atoms Mg, Li, and Ca due to the core hole ($\uparrow$), solid curve. The dashed lines describe the spin components of the ΔDOS or the screening. Note the different scaling in the case of Ca. The integrated area of each solid curve is 1.

ly calculated results is also made. The ionization phase shifts relevant to our values are tabulated in the Appendix. The agreement among all of these numbers in Table II is fairly good, though less satisfactory in the case of Na. The spurious singularity index 0.54 for the Na $2p$ hole in Ref. 6 probably arises from the s resonance formation.⁴⁰ It is therefore replaced in Table II by a value from Ref. 40. According to our results the double-hole states of Na and Mg bind $3s^2$ electrons. However, adding these to the final-state s -wave phases, each by the amount of π , we obtain the well-behaved transition phase shifts in the Appendix and, furthermore, the reported singularity indices for Auger lines. The generally accepted independence of the core level within the experimental errors is seen in the indices from Ref. 34. The numerical uncertainty in our calculated numbers could be estimated from the deviations in the Friedel sum of the transition phase shifts, but the core-hole self-energy errors and other core-level-dependent errors of our model are still unknown. Ignoring all this, our values seem to predict slightly more asymmetric photoelectron lines for the deep $1s$ hole than those for the L -shell holes. In order to compare the effect of the spin polarization the spin-symmetric estimations (ss) for the singularity indices were evaluated from the spin-averaged phase shifts $\delta_I = \frac{1}{2}(\delta_{I\uparrow} + \delta_{I\downarrow})$, but no deviations from

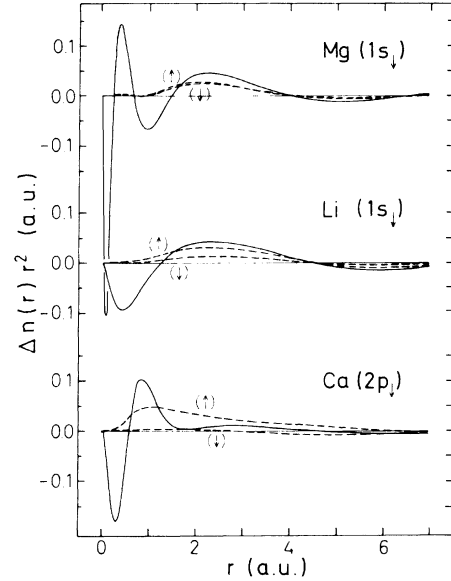


FIG. 3. Total change in radial charge density ($\Delta n(r)r^2$) including bound states for metal atoms Mg, Li, and Ca due to the core hole ($\uparrow$), solid curve. Thus the integrated area of each solid curve is 0. The dashed lines describe the spin components of the screening only and for these, 4π times the integrated area ($\uparrow + \downarrow$) is 1.

the spin-polarized values were found. As concluded from Eq. (7), the spin-symmetric value of α can generally be regarded as a lower limit for the corresponding spin-polarized value of α . In Table III the threshold exponents for the same elements and the same calculations are listed. The values for Na from Ref. 6 are again replaced by those from Ref. 40. According to our result the core-hole dependence is even weaker than that for singularity indices, and therefore only averages are given. The spin-symmetric values are given for comparison. General agreement between theory and experiment exists also in this case.

The shape of the Li K edge has previously been extensively discussed because of the discrepancy between theoretical and experimental results. The rounded edge shape from measurements^{34,36} predicts a large and negative α_1 . Such effects as large lifetime broadening, phonon broadening, or the shape of density of states near ϵ_F are suggested to explain this discrepancy.^{32,41,42} Although Li metal may be a special case with a large phonon broadening of the x-ray edge,⁴¹ according to the calculations of Almbladh⁴² similar effects should be present in Na and K metals. There seems to be, however, a difference between the screening of the core holes of Li and Na. Girvin and Hopfield suggested first that the spin of the screening charge may play an important

TABLE V. Singularity indices α and the threshold exponents α_l for Ca by the SDF method.

Core hole	α	α_0	Ca α_1	α_2	α_3	Method
2p	0.343	-0.43	-0.43	-0.38	-0.35	SDF
	0.146	-0.17	-0.19	0.09	-0.15	SDF (ss)
3p	0.355	-0.44	-0.45	-0.43	-0.36	SDF
	0.126	-0.13	-0.15	0.10	-0.13	SDF (ss)

role in these many-body effects.⁴³ This assumption is verified by our calculations: The s and p screenings are twice as large for the core-hole opposite spin compared to those of the core-hole parallel spin as seen from the phase shifts of Li given in the Appendix; see also Figs. 2 and 3. Almost equally strong spin polarization is found for the Be 1s hole screening. Girvin and Hopfield found an appreciable growth of the Li singularity index α due to the exchange effects, though their value is not compatible with the experiments; see Table IV. In our method the origin of the increasing spin polarization of the screening lies in the exchange and correlation interaction in local-density form, formulated by Gunnarsson and Lundqvist.⁴ Our results are also consistent with those in Ref. 24.

The SDF calculated values of α agree extremely well with the experimental value for Li of Ley *et al.*,³⁵ but for Be the agreement is not satisfactory. However, in both cases the theoretical values of Minnhagen are in agreement with ours. Our spin-averaged phase shifts yield singularity indices very similar to those of other density-functional values.^{5,6} The spin-symmetric values for the threshold exponents differ markedly from the SDF values that yield a negative $\alpha_1 = -0.06$. Other theoretical methods that also give a negative α_1 differ remarkably in the value of α_0 , which is, however, not measurable. This reflects a strict difference in the origin of the negative sign of α_1 . The negative α_1 of Mahan,³⁷ Lange,⁴⁴ or Ausman *et al.*³⁹ arises from the large s screening ($\alpha_0 \approx 0.4$) rather than spin-polarized screening. Girvin and Hopfield⁴³ argue both α_0 and α_1 to be close to zero, and this is satisfied only by the SDF values. The small number of experimental results restricts the full comparison of our values for Be. However, a conclusion of poor agreement can be drawn. In any case, spin-polarized calculations with core levels included can strongly be recommended for favorable interpretation of experiments. For example, the calculations of Leiro⁴⁵ using the difference of pseudopotentials again seem to overestimate the s screening, yielding a large α_0 .

Examples of the conduction-electron screening in energy space and in position space are shown in Figs. 2 and 3, respectively. In each case the spin components are shown separately to demonstrate the polarization effects. In Fig. 2 the s - and p -electron contributions for Mg and Li are not shown, but they are very much alike. The s contribution forms the cusp at lower energies, and the p contribution makes the hump closer to the Fermi level. In the case of Ca the screening is very localized and totally of d_1 type, as seen from the Appendix and as discussed later. Note the different scaling for the Δ DOS of Ca. In Fig. 3 the total change in radial charge density includes also the bound-electron states. Hence the created core hole and the atomic relaxation of other bound orbitals are clearly seen. Again, the shape of the Ca core hole (d_1) screening is seen to be different from those of Mg and Li, exhibiting forms of the diffuse atomic $3d_1$ orbital. This supports the idea of localization in the energy space seen in Fig. 2. It also causes the damping of the Friedel oscillations, which are seen for Mg and Li in the region displayed.

The totally spin-polarized screening of Ca increases the singularity index to more than double the spin-symmetric one, see Table V. Hence the predictions for extremely asymmetric XPS lines and broad x-ray edges can be made. There exist no published experimental data yet to verify these predictions, but these peculiarities will be discussed to a larger extent in a forthcoming paper⁴⁶ where the corresponding experimental results will be published.

To treat Auger transitions the double-hole final states were computed both with spins opposite and spins parallel. The double-hole states of Na, Mg, and Al have a bound $3s^2$ state in our jellium vacancy model. The eigenvalue of this level is of the order 0.6, 0.2, and 0.1 eV or less for Na, Mg, and Al, respectively. The radial charge distribution for these states is very diffuse, making the calculations elaborate. Sufficient convergence in the case of Al was not achieved, and hence the results are not reported. By applying Eq. (7) to evaluate the Auger line singularity indices, the values in Table VI are obtained. For comparison, both double-hole final-state spin components are also given. The configurational average³¹ is evaluated as described in Sec. II. This shows again the strong polarization of the additional screening of the Auger transition in Ca. The Auger spectrum of Ca, consisting of several very asymmetric lines close to each other, should have a strongly increasing intensity from higher to lower energies. In fact, this is experimentally verified.⁴⁶ The Na, Mg, or Ca Auger line shape should be quite similar to that of the XPS line, as seen by comparing Tables II, V, and VI.

TABLE VI. Auger line singularity indices α by the SDF method for Na, Mg, and Ca.

	Na($KL_{2,3}L_{2,3}$)	α Mg($KL_{2,3}L_{2,3}$)	Ca($L_{2,3}M_{2,3}M_{2,3}$)
$\uparrow\downarrow$ final state	0.135	0.107	0.310
$\uparrow\uparrow$ final state	0.142	0.106	0.398
Configurational			
average	0.138	0.106	0.345
ss average	0.134	0.105	0.116

The binding and Auger transition energies were evaluated as explained in Sec. II using configurational averages. The solid-state shifts were then evaluated from Eqs. (8) and (9); see Table VII. These types of calculations are discussed by Nieminen and Puska⁸ in detail, and a critical comparison to the experimental data is also made; thus we do not go through it in this paper. In general, the agreement is found to be better when compared to the other calculation methods cited in Ref. 8. However, owing to the atomiclike $3d$ screening of the Ca core hole(s), the excited-atom model²⁰ should be also valid. This is verified by our SDF free-atom and our Hartree-Fock calculations⁴⁷ that yield solid-state shifts 10.6 and 8.8 eV for the $2p$ photoelectron energy and 24.5 and 18.1 eV for the LMM Auger transition energy, respectively. Compared to the SDF jellium results of Table VII the spin-polarized method seems to overestimate the relaxation effect, whereas the spin-symmetric Hartree-Fock method gives values that are too low.

Let us further consider the two possible double p -hole final states of the Auger transition. The energy difference of these spin-hole states was earlier as-

signed to the multiplet splitting of the Auger spectra. Hence the change in this energy splitting may describe the change in the multiplet splitting in going from the free atom to solid state. In the case of Na and Mg the change is less than 10%, also experimentally verified for Mg (Ref. 49), but in the case of Ca the calculated energy splitting in the solid state is more than twice the splitting in the free atom. A possible reason is the strong overlap of $3p$ holes and spin-polarized d screening. This is further discussed in light of experimental results.⁴⁶

IV. SUMMARY AND CONCLUSIONS

We have presented SDF SCF *ab initio* calculations for metal and free atoms. From the metal results the photoemission and Auger electron line shapes and x-ray-edge shapes were obtained in terms of singularity index and edge exponent. The spin polarization of the screening was especially studied. Using the free-atom results as a reference the solid-state shifts relevant to photoemission and Auger transitions were further obtained.

TABLE VII. Solid-state shifts for the photoelectron (or binding) energies ΔE_{XPS} and the Auger electron energies ΔE_A by the SDF method compared to the experimental values from Ref. 22. The work function values Φ (Ref. 48) used in Eqs. (8) and (9). All values are in eV.

	Transition	Li	Be	Na	Mg	Al	Ca	
ΔE_{XPS}	1s	6.96	8.00	5.42	5.11	6.15		SDF
	2s			5.27	4.77	5.71		
	2p			5.25	4.80	5.74	9.42	
	3p						7.99	
	1s			4.9	4.9	6.3		expt.
ΔE_A	$KL_{2,3}L_{2,3}$			15.18	15.61	16.8 ^a		SDF
	$L_{2,3}M_{2,3}M_{2,3}$						19.87	
	$KL_{2,3}L_{2,3}$			14.3	15.0	16.9		expt.
Φ		2.93	4.98	2.36	3.66	4.28	2.87	expt.

^aFrom Ref. 8.

TABLE VIII. Some values of the transition phase shifts and the corresponding deviations ΔF of the Friedel sum from its exact-value one. The spin-hole occupation is indicated by a negative superscript. g.s. denotes ground states.

Element Spin		δ_0	δ_1	δ_2	ΔF	δ_0	δ_1	δ_2	ΔF	δ_0	δ_1	δ_2	ΔF
		g.s. $\rightarrow 1s_i^{-1}$				$1s_i^{-1}\rightarrow 2p_i^{-1}p_i^{-1}$				$1s_i^{-1}\rightarrow 2p_i^{-2}$			
Li	$\uparrow$	0.73	0.57	-0.03	+ 0.003								
	$\downarrow$	0.38	0.20	-0.03									
Be	$\uparrow$	0.44	0.50	0.00	-0.008								
	$\downarrow$	0.27	0.31	0.00									
Na	$\uparrow$	0.77	0.32	-0.01	+ 0.007	0.37	0.40	-0.01	+ 0.012	0.41	0.53	-0.01	+ 0.013
	$\downarrow$	0.72	0.28	-0.01		0.42	0.43	-0.01		0.36	0.30	-0.01	
Mg	$\uparrow$	0.52	0.38	0.00	-0.005	0.26	0.36	0.02	-0.021	0.30	0.44	0.02	-0.053
	$\downarrow$	0.48	0.34	0.00		0.31	0.40	0.02		0.26	0.32	0.02	
Al	$\uparrow$	0.39	0.41	0.01	+ 0.006								
	$\downarrow$	0.36	0.37	0.01									
		δ_0	δ_1	δ_2	δ_3	ΔF	δ_0	δ_1	δ_2	δ_3	ΔF		
		g.s. $\rightarrow 2p_i^{-1}$					g.s. $\rightarrow 3p_i^{-1}$						
Ca	$\uparrow$	0.07	0.02	0.81	-0.01	+ 0.001	0.14	0.06	0.82	-0.01	-0.017		
	$\downarrow$	-0.14	-0.14	-0.06	-0.01		-0.14	-0.15	-0.11	-0.01			
		$2p_i^{-1}\rightarrow 3p_i^{-1}p_i^{-1}$					$2p_i^{-1}\rightarrow 3p_i^{-2}$						
Ca	$\uparrow$	-0.06	-0.10	-0.10	-0.01	-0.025	0.07	0.04	0.86	-0.00	-0.015		
	$\downarrow$	0.15	0.05	0.77	-0.01		-0.25	-0.12	-0.17	0.01			

The screening response of the conduction electrons to the core hole(s) in Na, Mg, or Al was found to be spin-symmetric, supporting previous results also in good agreement with experimental results. However, the slight core-level dependence of the singularity index can be predicted though not experimentally confirmed due to the experimental uncertainty. The screening of the $1s$ core hole of Li or Be is strongly spin-polarized, resulting in both an increase of the singularity index and a decrease of the edge exponents. This yields negative α_1 for the K edge of Li, which is also experimentally observable, whereas previously calculated negative values for Li α_1 arise from the overestimated s -screening contribution rather than the spin polarization of the screening.

The screening of the $2p$ or $3p$ core hole in Ca is localized in energy, totally spin-polarized, and very similar to the atomic $3d$ orbital in shape. This causes an anomalously large positive singularity index and negative threshold exponents. The lack of experimental data for Ca at this time prevents the verification of our predictions. For each element considered, the Auger line shape should be similar to the core-level photoelectron line shape.

The solid-state shifts for the transitions considered were also evaluated. Agreement with the ex-

perimental results is found to be good.⁸ The shift values are considerable for Li and Be, and for Ca they are exceptionally large. The latter is explained by the atomiclike localization of the screening charge. This was verified also by the excited-atom calculations.

As a final conclusion, a spin-polarized method can be strongly recommended for the conduction-electron screening calculations for a core hole in Li or Be, and for a core hole in Ca it seems to be necessary.

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APPENDIX

We present values of ionization phase shifts relevant to our values in Table VIII.

- ¹P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- ²W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- ³U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
- ⁴O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
- ⁵C.-O. Almbladh and U. von Barth, Phys. Rev. B **13**, 3307 (1976).
- ⁶G. W. Bryant and G. D. Mahan, Phys. Rev. B **17**, 1744 (1978).
- ⁷N. D. Lang and A. R. Williams, Phys. Rev. B **20**, 1369 (1979); A. R. Williams and N. D. Lang, Phys. Rev. Lett. **40**, 954 (1978).
- ⁸R. M. Nieminen and M. J. Puska, Phys. Rev. B **25**, 67 (1982).
- ⁹U. von Barth, Phys. Rev. A **20**, 1693 (1979); J. H. Wood, J. Phys. B **13**, 1 (1980); M. Lannoo, G. A. Baraff, and M. Schlüter, Phys. Rev. B **24**, 943 (1981).
- ¹⁰M. Manninen, P. Hautojärvi, and R. Nieminen, Solid State Commun. **23**, 795 (1977); R. M. Nieminen and M. J. Puska, J. Phys. F **10**, L123 (1980).
- ¹¹M. J. Puska, R. M. Nieminen, and M. Manninen, Phys. Rev. B **24**, 3037 (1981).
- ¹²G. W. Bryant, Phys. Rev. B **19**, 2801 (1979); **19**, 2864 (1979).
- ¹³N. D. Lang and A. R. Williams, Phys. Rev. B **16**, 2408 (1977); Phys. Rev. Lett. **34**, 531 (1975); **37**, 212 (1976).
- ¹⁴N. D. Lang, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1973), Vol. 28, p. 225.
- ¹⁵R. M. Nieminen, J. Phys. F **7**, 375 (1977).
- ¹⁶See, e.g., *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971).
- ¹⁷G. D. Mahan, Phys. Rev. **163**, 612 (1967).
- ¹⁸P. Nozières and C. T. De Dominicis, Phys. Rev. **178**, 1097 (1969).
- ¹⁹D. A. Shirley, Phys. Rev. A **7**, 1520 (1973); L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B **8**, 2392 (1973).
- ²⁰R. E. Watson, M. L. Perlman, and J. F. Herbst, Phys. Rev. B **13**, 2358 (1976); M. Pessa, A. Vuoristo, M. Vulli, S. Aksela, J. Värynen, T. T. Rantala, and H. Aksela, *ibid.* B **20**, 3115 (1979).
- ²¹B. Johansson and N. Mårtensson, Phys. Rev. B **21**, 4427 (1980); P. Steiner, N. Hüfner, N. Mårtensson, and B. Johansson, Solid State Commun. **37**, 73 (1981).
- ²²S. Aksela, R. Kumpula, H. Aksela, and J. Värynen, Phys. Scr. **25**, 45 (1982).
- ²³S. Aksela, R. Kumpula, H. Aksela, J. Värynen, R. M. Nieminen, and M. Puska, Phys. Rev. B **23**, 4362 (1981).
- ²⁴After submitting the manuscript it came to the author's knowledge that spin-polarized phase shifts have been previously reported by C.-O. Almbladh and U. von Barth, in *Proceedings of the 5th International Conference on Vacuum Ultraviolet Radiation Physics* (Montpellier, France, 1977) and *Proceedings of the 8th International Symposium on Electronic Structure of Metals and Alloys* (Gaussig, East Germany, 1978).
- ²⁵R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1963).
- ²⁶F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., New Jersey, 1963).
- ²⁷NAG FORTRAN Library Mark 8 (Numerical Algorithms Group, Oxford, 1981).
- ²⁸M. Combescot and P. Nozières, J. Phys. (Paris) **32**, 913 (1971).
- ²⁹S. Doniach and M. Sunjić, J. Phys. C **3**, 285 (1970).
- ³⁰J. Friedel, Philos. Mag. **43**, 153 (1952).
- ³¹J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vols. I and II.
- ³²G. K. Wertheim and P. H. Citrin, in *Topics in Applied Physics*, edited by M. Cardona and L. Ley (Springer, Berlin, 1978), Vol. 26, p. 197.
- ³³P. Steiner, H. Höchst, and S. Hüfner, Z. Phys. B **30**, 129 (1978); H. Höchst, P. Steiner, and S. Hüfner, Phys. Lett. **60A**, 69 (1977).
- ³⁴P. H. Citrin, G. K. Wertheim, and Y. Baer, Phys. Rev. B **16**, 4256 (1977); Phys. Rev. Lett. **35**, 885 (1975); Y. Baer, P. H. Citrin, and G. K. Wertheim, *ibid.* **37**, 49 (1976).
- ³⁵L. Ley, F. R. McFeely, S. P. Kowalczyk, J. G. Jenkin, and D. A. Shirley, Phys. Rev. B **11**, 600 (1975).
- ³⁶J. D. Dow and B. F. Sonntag, Phys. Rev. Lett. **31**, 1461 (1973).
- ³⁷G. D. Mahan, Phys. Rev. B **11**, 4814 (1975).
- ³⁸P. Minnhagen, Phys. Lett. **56A**, 327 (1976).
- ³⁹G. A. Ausman, Jr., and A. J. Glick, Phys. Rev. **183**, 687 (1969).
- ⁴⁰G. W. Bryant, J. Phys. F **10**, 321 (1980).
- ⁴¹G. D. Mahan, Phys. Rev. B **15**, 4587 (1977).
- ⁴²C.-O. Almbladh, Phys. Rev. B **16**, 4343 (1977).
- ⁴³S. M. Girvin and J. J. Hopfield, Phys. Rev. Lett. **37**, 1091 (1976).
- ⁴⁴P. Longe, Phys. Rev. B **8**, 2572 (1973).
- ⁴⁵J. A. Leiro, Solid State Commun. **41**, 97 (1982).
- ⁴⁶J. Värynen, T. T. Rantala, E. Minni, and E. Suoninen, J. Electron Spectrosc. **31** (1983).
- ⁴⁷C. Froese-Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).
- ⁴⁸Tabulations by J. Hölzl and F. K. Schulte, in *Solid Surface Physics*, Vol. 85 of *Springer Tracts in Modern Physics* (Springer, Heidelberg, 1979).
- ⁴⁹J. Värynen, S. Aksela, and H. Aksela, Phys. Scr. **16**, 452 (1977).