The spherical-solid model: An application to x-ray edges in Li, Na, and Al[†]

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(Received 14 July 1975)

In order to treat highly localized excitations in a solid a simple spherical model has been developed. The Coulomb potential from the nucleus at the site of the excitation is treated exactly, while the potentials from the surrounding sites are turned into pseudoion pontentials. Only the spherical average of these potentials is retained and separate self-consistent calculations for the ground state and for the excited state are made. These states are mistreated by the model but the difference accurately describes the large effects of polarization involved. The positions of the x-ray edges are obtained with an accuracy of 0.5 eV for singly ionized levels and 1 eV for doubly ionized levels. The phase shifts relevant to the Nozières–De Dominicis theory of x-ray absorption and emission edges and x-ray photoemission line shapes are also calculated. We obtain a noticeable many-body enhancement of the $L_{2,3}$ edge in Na while the many-body effect in Li and Al is negligible. Our exponents agree with those extracted from recent x-ray photoemission experiments, but they do not agree with those extracted from x-ray emission or absorption spectra. We argue that the exponents taken from the photoemission experiment are more reliable but no definite conclusion concerning the validity of the present many-body theory should be drawn until the experimental situation has become more clear.

I. INTRODUCTION

In this paper we develop a scheme called the "spherical-solid model" (SSM) to treat the impurity problem in simpler metals. In general the impurity problem is very difficult to handle, the main reason being the fact that the translational symmetry, so convenient in band-structure calculations, is broken. The problem is especially hard when the effect of the impurity extends far out into the host crystal. This is the case if the radius of the impurity atom is appreciably different from the radius of the host atoms and one is faced with the problem of lattice relaxation. Even in the case of deep impurities in semiconductors the impurity wave function can have a large amplitude on the nearest host atoms.[1] In order to get reasonable results for this problem one probably has to resort to cluster calculations. However, the class of problems we propose to treat with our model has to be such that the wave functions bound to the impurity vanish within a distance less than the nearest-neighbor distance, and such that the induced effect of the impurity rapidly dies off outside the central Wigner-Seitz cell. The physical content of the model can be described in simple terms. We picture ourselves as sitting at the center of the impurity atom and looking at the surroundings. Assuming the electrons on the impurity atom to feel only the average field of the remainder of the crystal, we rotate the whole crystal around the center. The nuclear charges of the host atoms are thus uniformly spread out on spherical shells. The Coulomb potential from these shells is, however, not strong enough to bind the core electrons sufficiently tightly to the shells. To overcome this difficulty we modify our

model by taking the spherical average of the potential from the surrounding nuclei and their attached core electrons. The whole system with the exception of these core electrons is then allowed to relax in this potential. Our model is thus completely spherical. We think, however, that there is a number of problems to which the SSM should be a comparatively accurate approach. The residual resistivity of dilute liquid-metal alloys and the Mott-type α-γ transition in cerium[2] are probably good examples.

We have chosen to test the model in a calculation of threshold energies of x-ray absorption and emission spectra from simple metals. The threshold energy for, e.g., x-ray absorption is the energy of a transition from the ground state of the system to the lowest possible state with one core hole present. The core electron spectral function $A_c(\omega)$ gives the probability distribution for excitation energies of the system with the core hole.[3] Thus $A_c(\omega)$ vanishes below the threshold energy, and consequently this energy (but not the shape of the spectrum) can be obtained from a knowledge of the core-electron self-energy. Using a simplified version of the dynamically screened exchange approximation[3] (the GW approximation) for the self-energy, Hedin[4] succeeded in reproducing the core levels of a number of simpler metals with an accuracy of about 1.0–1.5 eV. Considering the crude estimates made by Hedin for the very large Hartree contribution and for the chemical potential, the accuracy is indeed good. Still better agreement with experiments is most likely obtained by using a more realistic screening function and a better Green's function with some good Bloch functions of the crystal. To make such a large effort worthwhile, our analysis shows that

some estimate of the nonlinear effects must be
made, i.e., some estimate of the next higher or-
der diagram in the expansion of the self-energy in
screened interaction has to be added to the linear
approximation.

In the present work we have chosen to approxi-
mate the self-energy using the so-called[5] ΔSCF
method in which the threshold energy is taken as
the difference in total energies of two self-consis-
tent field (SCF) calculations, one for the ground
state of the system and one for a state with a core
hole and an extra electron at the Fermi level. The
advantage of this method is that it contains a pos-
sibility to treat the relaxation energy of the va-
lence electrons in a nonlinear fashion. This rep-
resents a considerable improvement on the GW
approximation since the nonlinear effects can
amount to 1 eV for singly ionized levels. For
doubly ionized levels the effect is four times larg-
er. On the other hand, the ΔSCF method neglects
some dynamical effects included in the GW approxi-
mation which may be important for shallow core
levels.

In a Kohn-Sham ΔSCF calculation performed in
the present work another difficulty arises from
the fact that there is no theoretical justification
for obtaining the total energy for the excited state
from a self-consistent calculation with an empty
core state. In as much as the core hole can be
treated as an external potential, the method should
however be physically sound. In addition, the
ΔSCF method takes some core-valence exchange
into account.

Flynn and Lipari[6] used an approximate form of
the ΔSCF method and obtained reasonable results.
Their theory has, however, several deficiencies.
(a) They resorted to pseudopotential theory to ob-
tain the difference in relaxation energies of the
electron gas with and without core hole. In the
case of lithium they state that small changes in
the pseudopotential parameters can cause changes
in the final result of the order of several eV. (b)
They used linear-response theory to obtain the en-
ergy of the screening cloud associated with the
core-hole potential. The resulting error was
partly compensated for by using the bare core-hole
potential instead of a pseudopotential which would
have been more appropriate in the context of their
theory. (c) Their core states were allowed to re-
lax in the field of the electron-gas pseudo charge
density, which should be bad in the core region. (d)
They neglect exchange between core and valence elec-
trons. In Al this gives an error of 0.7 eV.[3]

Using pseudopotential techniques Flynn and
Lipari took due account of lattice symmetry. For
our purposes an important conclusion of their
work is that the threshold energy is quite insen-
sitive to crystal symmetry.

Recently the relevance of many-body theory to
the shape of the soft-x-ray edges in simple metals
has been extensively debated.[7-10] According to
Nozières and De Dominicis[11] the shape of the edges
obeys a power law with an exponent that in a spher-
ical model is determined by the Fermi-level phase
shifts of the screened potential from the core hole.
Since we do spherical self-consistent calculations
both for the ground state and for the state with the
core hole present, we are in a unique position to
obtain the phase shifts relevant to the Nozière-De
Dominicis theory. The SSM takes due account of
ionic structure and hence there is no longer a
need for pseudopotential fitting schemes.[7] More-
over, no adjustable parameter enters in the de-
scription of screening. To judge from our results
for the threshold energies both the effect of non-
linearity, and the influence of the ionic core on the
screening of the core hole are accurately accounted
for by the SSM. Our hope is hence that this work
will shed some light on the present controversy.

II. THEORY

A. Model

We start by writing down the equations relevant
for the Kohn-Sham theory[12,13] in its local density
form

$$\left(-\tfrac{1}{2}\nabla^2 + w(\vec{r}) + \int \rho(\vec{r}')v(\vec{r}-\vec{r}')\,d^3r' + \mu_{xc}(\rho(\vec{r}))\right)\varphi_i(\vec{r})$$
$$= \mathscr{E}_i\varphi_i(\vec{r}), \quad (1)$$

$$\rho(\vec{r}) = \sum_{\mathscr{E}_i<\mathscr{E}_F}|\varphi_i(\vec{r})|^2 ; \quad N = \sum_{\mathscr{E}_i<\mathscr{E}_F}1 . \quad (2)$$

Here $v(\vec{r}) = 1/r$ is the Coulomb interaction; N is
the total number of electrons in the system. We
use atomic units (energies in Hartree = 27.21 eV)
unless otherwise stated. $\mu_{xc}(\rho)$ is the exchange
correlation contribution to the chemical potential
of the homogeneous electron gas of density ρ. For
μ_{xc} we use the parametrization of Hedin and Lund-
qvist[14] as modified by Arbman and von Barth.[15]
$w(\vec{r})$ should be the potential from all nuclei:

$$w(\vec{r}) = -\sum_{\vec{l}}\frac{Z}{|\vec{r}-\vec{l}|} , \quad (3)$$

where Z is the atomic number and $\vec{l}$ are the vec-
tors of the direct lattice. For the reasons given
in the introduction the potential from the central
nucleus ($\vec{l} = 0$) is treated exactly while in the po-
tential from the surrounding sites we include the
potential from their respective core electrons.
Thus

$$w(\vec{r}) = -\frac{Z}{r} + \sum_{\vec{l}\neq 0}w_0(\vec{r}-\vec{l}) , \quad (4)$$

where $w_0(\vec{r})$ is $-Z/r$ plus the potential from the

core electrons on one site. Accordingly, $w_0(\vec{r})$ will behave as $-Z_v/r$ for large r, Z_v being the valency. Our next approximation is to retain only the spherical average $w(r)$ of the external potential $w(\vec{r})$,

$$w(r) = \int \frac{d\Omega}{4\pi}\, w(\vec{r}) \; . \tag{5}$$

The spherical averaging is most easily accomplished in Fourier space. After some algebra we obtain

$$w(r) = -\frac{Z}{r} - \int \rho_0 v(\vec{r} - \vec{r}')\, d^3 r' + W_0$$

$$+ \frac{1}{\Omega_0} \sum_{\vec{G} \neq 0} w_0(G)\, \frac{\sin Gr}{Gr} - w_0(r) \; . \tag{6}$$

Here Ω_0 is the volume of the unit cell, ρ_0 is the average valence electron density, $\rho_0 = Z_v/\Omega_0$, $\vec{G}$ is a vector of the reciprocal lattice, $w_0(G)$ is the Fourier transform of $w_0(r)$, and W_0 is some finite constant. Shifting the energy eigenvalues in Eq. (1) by the constant $\mathcal{E}_0 = W_0 + \mu_{xc}(\rho_0)$, $\epsilon_i = \mathcal{E}_i - \mathcal{E}_0$, Eq. (1) can be rewritten

$$\left[-\tfrac{1}{2}\nabla^2 + V(r) + V_H(r) + V_{xc}(r)\right] \varphi_i(\vec{r}) = \epsilon_i \varphi_i(r) \; , \tag{7}$$

where

$$V(r) = -\frac{Z}{r} + \frac{1}{\Omega_0} \sum_{\vec{G} \neq 0} w_0(G)\, \frac{\sin Gr}{Gr} - w_0(r) \; , \tag{8}$$

$$V_H(r) = \int \left[\rho(\vec{r}') - \rho_0\right] v(\vec{r} - \vec{r}')\, d^3 r' \; , \tag{9}$$

$$V_{xc}(r) = \mu_{xc}(\rho(r)) - \mu_{xc}(\rho_0) \; . \tag{10}$$

The underlying assumption in this work is the insensitivity of the electrons in the central cell to finer details of the charge distribution on the surrounding sites. Pursuing this idea we finally approximate the potential $w_0(r)$ by a convenient analytic expression having the correct behavior at large distances ($w_0 \simeq -Z_v/r$) and simulating some of the repulsive effect of core orthogonality. We choose

$$w_0(r) = -(Z_v/r)\, \mathrm{erf}(r/r_c) \tag{11}$$

and hence

$$w_0(G) = -Z_v(4\pi/G^2)\exp(-\tfrac{1}{4}r_c^2 G^2) \; . \tag{12}$$

The constant r_c is determined by requiring the approximate $w_0(r)$ to have the same effect, with regard to charge densities at large distances, as the true potential $w_0(r)$. Suppose the Eqs. (2) and (7)–(10) have been solved self-consistently for the charge density $\rho(r)$ using some value for r_c. The potential from the central nucleus and from the core electrons on the central atom can then be replaced by the approximate $w_0(r)$, and we can solve for a second valence density $\rho'(r)$. The "correct"

value for r_c is characterized by having $\rho(r) \simeq \rho'(r)$ well outside the radius r_c. It turns out that there exists a "correct" value for r_c, showing the approximation (11) to be reasonable, and that this value can be obtained from an iterative procedure. We want to stress that the approximate potential $w_0(G)$ should not be confused with common model pseudopotentials obtained by fitting to spectral data for the ion. It is merely a convenient numerical tool to avoid the Fourier transform of the true potential $w_0(r)$.

It should be noted that the Eqs. (2) and (7)–(11) were previously treated by Dagens,[16] although derived differently and used for other purposes. In the work of Dagens the lattice part of the potential, i.e., the second terms in Eq. (8) and the core electrons were not included in the self-consistency loop, but a correction for the lattice was added on afterwards as a perturbation. The r_c values used by Dagens were also quite different from ours.

The full problem in Eq. (1) has now been transformed to a problem equivalent to a disturbance $V(r)$ in an originally homogeneous electron gas of density ρ_0. Because of screening the total potential $V + V_H + V_{xc}$ will tend to zero faster than $1/r$, and hence the Fermi energy will be the same as for free particles, i.e.,

$$\epsilon_F = \mathcal{E}_F - \mathcal{E}_0 = \tfrac{1}{2}k_F^2 = (3\pi^2\rho_0)^{2/3} \; . \tag{13}$$

Equation (7) is integrated outwards to a radius R large enough to obtain an adequate description of the physics of the central cell. However, we consider the system to be infinite and the normalization condition on the wave functions only enters via an arbitrary choice of density-of-states function.

In Kohn-Sham theory the total energy of an electron gas subject to the external potential V is given by

$$E_V[\rho] = T_S[\rho] + \frac{1}{2}\int\int (\rho - \rho_0)\, v(\rho - \rho_0)$$

$$+ \int V(\rho - \rho_0) + \int \rho \epsilon_{xc}(\rho) \; , \tag{14}$$

where $T_S[\rho]$ is the kinetic energy of a system of noninteracting particles having the density ρ, $\epsilon_{xc}(\rho)$ is the exchange-correlation energy per particle of a homogeneous electron gas of density ρ, and integrations are running over all space. Since we are interested in differences between excited and ground-state energies we can measure energies relative to an fixed energy, and to avoid infinite quantities we choose $E_V[\rho_0]$. Thus with

$$E_V'[\rho] = E_V[\rho] - E_V[\rho_0] \; ,$$

we have

$$E'_V[\rho] = T_S[\rho] - T_S[\rho_0] + \frac{1}{2} \int \int (\rho - \rho_0) v(\rho - \rho_0)$$

$$+ \int V(\rho - \rho_0) + \int \rho \epsilon_{xc} - \int \rho_0 \epsilon_{xc}^0 , \qquad (15)$$

where $\epsilon_{xc}^0 = \epsilon_{xc}(\rho_0)$. $T_S[\rho] - T_S[\rho_0]$ is easily obtained directly from Eq. (7) giving

$$T_S[\rho] - T_S[\rho_0] = \sum_c \epsilon_c + \epsilon_F Z_F(\epsilon_F)$$

$$- \int_0^{\epsilon_F} Z_F(\epsilon) d\epsilon - \int \rho(V + V_H + V_{xc}) , \qquad (16)$$

where

$$Z_F(\epsilon) = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l + 1) \delta_l(\epsilon) , \qquad (17)$$

ϵ_c are the bound-state energies and $\delta_l(\epsilon)$ are the phase shifts defined to be zero for infinite energy $[\delta_l(\epsilon) \to 0, \epsilon \to \infty]$. According to Eqs. (8) and (11) $V(r)$ behaves as $(Z_v - Z)/r$ for large r. Thus, if N_c is the number of occupied bound states, the Friedel sum rule states that

$$Z - Z_v = Z_F(\epsilon_F) - Z_F(0) + N_c . \qquad (18)$$

Note that for filled shells of bound states $N_c = Z_F(0)$. The second term $V_2(r)$, of the right-hand side of Eq. (8) can be thought of as generated by a charge distribution $- \nabla^2 V_2(r)/4\pi$. The total amount of charge $Q_2(r)$ inside a radius r of this charge distribution, is a very slowly decreasing function of r. Since we interrupt the outward integration at some large but finite radius R, $Q_2(R)$ is a measure of to what accuracy the Friedel sum rule can be obtained $[Q_2(R) \sim 0.1]$. However, the errors cancel when we take differences in total energies of the ground and excited states. Indeed the difference phase shifts obey the Friedel sum with a high

TABLE I. Nonlocality corrections for free-ion core energies. Here av indicates the average over the relevant configuration or term. Experimental numbers from Ref. 17.

Transition	Experiment	ΔSCF–KS	Correction
$Na^{2+}\ 2p^5av - Na^{1+}\ 2p^6$	47.4	48.5	−1.1
$Al^{4+}\ 2p^5av - Al^{3+}\ 2p^6$	120.1	121.2	−1.1
$Na^{3+}\ 2p^4av - Na^{2+}\ 2p^5av$	73.5	74.5	−1.0
$Al^{5+}\ 2p^4av - Al^{4+}\ 2p^5av$	156.2	157.2	−1.0
$Na^{3+}\ 2p^4av - 2p^4\ {}^3P_{av}$	1.8	⋯	−1.8
$Al^{5+}\ 2p^4av - 2p^4\ {}^3P_{av}$	2.4	⋯	−2.4
$Li^{2+}\ 1s^1 - Li^{1+}\ 1s^2$	75.6	78.2	−2.6
$Al^{12+}\ 1s^1 - Al^{11+}\ 1s^2$	2086	2089	−3
$Li^{3+}\ 1s^0 - Li^{2+}\ 1s^1$	122.5	116.3	6.2

accuracy (Table IV) showing that outside the radius R the effect of the core hole(s) is negligible.

B. Atomic corrections

The ΔSCF Kohn-Sham (KS) theory should give an exact answer for the energy required to strip one electron from a free ion provided the "exact" exchange-correlation potential is used. Owing to the large inhomogeneties in an ion the local density approximation used by us for this potential introduces an error of the order of 1 eV. Our model is rather designed to give a good description of the less inhomogeneous and electron-gas-like polarization effects involved in the excitation process. To allow for an accurate comparison to experimental results we will, however, add an atomic nonlocality correction to our ΔSCF results.

The correction for an $L_{2,3}$ threshold is obtained as the difference between a spherical ΔSCF-Kohn-Sham calculation for the atomic transition $1s^2 2s^2 2p^6 \to 1s^2 2s^2 2p^5$ and the configurational average of the experimental energies $E(p^6, {}^1S_0 \to p^5, {}^2P_{1/2})$ and $E(p^6, {}^1S_0 \to p^5, {}^2P_{3/2})$ for the same transition in the relevant free ion.[17] We should thus compare our final results to the configurational average of the experimental L_2 and L_3 thresholds in the metal. The calculated and experimental results for the atomic transitions and the corresponding corrections can be studied in Table I.

For a K threshold the correction is obtained in the same way $(1s^2 \to 1s)$ but of course without configurational averaging since only one atomic state is involved. Owing to the poor description of one- and two-electron systems offered by the paramagnetic Kohn-Sham theory the correction is much larger in this case. Adding the correction to the solid-state calculation we implicitly assume it to be independent of the surroundings, an approximation that might be too crude for such a large correction. This is most likely the reason why the result for singly ionized Li is slightly worse than those for Na and Al. Note that for the K edge in Al we only correct for the nonlocality effects in the K shell. The relaxation of the L shell is taken care of by our ΔSCF calculation. This explains the 3-eV discrepancy (Table II) between theory and experiment for the K edge in Al, because the Kohn-Sham local density theory is probably not accurate enough to account for this large atomic relaxation effect.

For the emission edge of doubly ionized core levels the situation is complicated by the fact that an atomic p^4 configuration produces six different atomic levels: ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, ${}^1D_2$, and ${}^1S_0$. The spread in the ${}^3P$ levels is a consequence of spin-orbit interaction and is only 0.2 eV in Na and 0.5

TABLE II. X-ray threshold energies (eV). E_1 is the energy of the main band threshold and E_2 is energy of the satellite threshold. The ΔSCF–KS energies contain atomic corrections from Table I and the experimental energies are spin averages.

	Na $L_{2,3}$		Al $L_{2,3}$		Li K		Al K
	E_1	$E_2 - E_1$	E_1	$E_2 - E_1$	E_1	$E_2 - E_1$	E_1
ΔSCF–KS	30.5	12.3	72.7	15.1	55.5	29.1	1557
Experiment	30.4[a]	11.3[c]	72.9[b]	15.7[b]	54.8[a]	28.8[d]	1560[e]

[a]Kunz, Ref. 35.   [d]Bedo et al., Ref. 41.
[b]Neddermeyer et al., Ref. 24.   [e]Neddermeyer, Ref. 42.
[c]Hanson et al., Ref. 25.

eV in Al. In any case the splittings are not resolved experimentally and in analogy with the p^5 configuration we consider the ^3P levels as one level having the energy of their average ($^3P_{av}$). However, the splittings caused by the Coulomb interaction between the terms ^3P, ^1D, and ^1S are large[17] (3.8 and 4.4 eV in Na and 5.0 and 5.8 eV in Al) and must be taken into account before a comparison with experiments is made. Our ΔSCF calculation gives the energy for the transition between two configurational averages ($p^4_{av} - p^5_{av}$). Experimentally the threshold energy for emission from doubly ionized $2p$ core states is the energy of the transition $2p^4, {}^3P_{av} \rightarrow 2p^5, {}^2P_{av}$, since this transition is not forbidden by symmetry, since $^3P_{av}$ is the lowest of the terms ^3P, ^1D, and ^1S and since the emission at threshold should start from the fully relaxed "ground state" with two core holes present.

This assignment of the double ionization satellite is supported by experimental data on the $K\alpha_3$ and[18] $K\beta^{III}$ satellites in the Al, Mg, and Na x-ray spectra. The data allow an independent way of determining the $LL(2p^4, {}^3P)$ energy in the metals. According to Horak[19] the $K\alpha_3$ satellite corresponds to the transition $KL_{2,3}(1s^1 2p^5, {}^3P) \rightarrow LL(2p^4, {}^3P)$, while the edge of the $K\beta^{III}$ satellite corresponds to the transition $KL_{2,3}(1s^1 2p^5, {}^3P) \rightarrow L_{2,3}(2p^5 \epsilon_F v)$. If the high-energy satellite in the L spectrum corresponds to the ^3P term the energy E_2 of the satellite edge should equal the energy difference ΔE_K between the $K\alpha_3$ satellite and the edge of the $K\beta^{III}$ satellite. Using Tyrén's[20] data on the $K\alpha_3$ satellites and Karlsson and Siegbahn's[21] data on the $K\beta^{III}$ satellites we obtain $\Delta E_K = 88.4$, 63.1, and 41.4 eV in Al, Mg and Na, respectively.[22] These numbers are in strikingly good agreement with the experimental numbers $E_2 = 88.6$, 63.5, and 41.7 eV taken from Neddermeyer and Wiech[24] (Al) and Hanson and Arakawa[25] (Mg and Na).

The assignment is further supported by recent KLL Auger experiments on[26] Mg and[27] Na. These experiments claim to give the energy E_{KLL} rela-

tive to the Fermi energy of the transition $K(1s^1 2p^6) \rightarrow LL(2p^4, {}^1D)$. Thus subtracting the energy E_{KLL} from the energy $E_{K\alpha}$ of the $K\alpha$ x-ray line taken from the same references, we obtain the energy of the transition $LL(2p^4, {}^1D)-L_{2,3}(2p^5 \epsilon_F v)$. By further subtracting the $^3P-{}^1D$ atomic term splitting which amounts to 4.4 eV in Mg and 3.8 eV in Na,[17] the energy of the transition $LL(2p^4, {}^3P)-L_{2,3}(2p^5 \epsilon_F v)$ is found to be 63.6 eV in Mg and 43.3 eV in Na. These energies are in fairly close agreement with the experimental E_2 energies. The 1.6-eV discrepancy in Na is probably due to experimental errors but is anyway less than the atomic term splitting.

Thus our ΔSCF results have to be corrected both for the difference between the experimental and Kohn-Sham configurational averages for the transition $p^4 \rightarrow p^5$, and for the difference between the experimental $2p^4, {}^3P_{av}$ and $2p^4_{av}$ energies (see Table I). In the case of the doubly ionized K hole in Li only the first correction is applicable since only one atomic level is involved.

III. RESULTS

A. Threshold energies

Our calculated x-ray threshold energies and the threshold energies of the corresponding satellites due to double ionization are compared to experimental results in Table II. The agreement is indeed gratifying and verifies our basic assumption of the insensitivity of the threshold energies with regard to crystal symmetry. The slightly lower accuracies obtained for the K edges in Li and Al were discussed in Sec. II. The satellite peak in sodium is off by 1 eV as compared to the data by Hanson et al.[25] The experimental situation seems however to be somewhat uncertain in this case, e.g., Skinner[28] obtains 11.9 eV which is much closer to our result. The discrepancy can partly be explained by insufficient numerical accuracy. With two $2p$ holes present in Na the self-consistent potential is so strong, due to a relatively

large r_s ($r_s = 4$), that the Kohn-Sham "ground state" contains a doubly occupied bound valence state ($3s^2$). The one-electron energy of this state is very small (0.045 Ry) causing the bound-state wave function to be spread out. The radial integration thus has to be carried far out, and breaking it off too soon tends to give a total energy that is too high. The error due to this effect is however certainly smaller than 0.5 eV. In all other cases we estimate the over-all numerical error in the threshold energies to be less than 0.3 eV. There are essentially five numerical parameters on which our results can depend. These are the maximum radius R outside which the effect of the core hole(s) was considered to be negligible, the parameter r_c in the potential $w_0(r)$, the maximum l quantum number (l_{max}), the number of energy mesh points (N_ϵ) in the continuum and the number of mesh points (N) for the radial integration. We increased l_{max}, N_ϵ, and N until the threshold energies were converged within 0.05 eV. For, e.g., Al this occurred at $l_{max} = 13$, $N_\epsilon = 20$, and $N = 231$. In order for the approximation, of replacing the core potential on the neighboring sites by model potentials with a parameter r_c, to be reasonable, the threshold energies E_t should be insensitive to the choice of r_c. To check this, we evaluated dE_t/dr_c in the case of Al and obtained 0.6 eV/a.u. Since the self-consistent determination of r_c, described in Sec. II A, has an accuracy better than 0.2 a.u., the error in E_t from the model potential procedure is less than 0.1 eV. The dependence of E_t on R is, however, more severe. Far out from the center the external potential $V(r)$ has a slow sinusoidal type variation and the valence electron density [$\rho^v(r)$] closely follows this variation. The largest change in E_t with R should therefore occur for two R values lying at two consecutive nodes of $\rho^v(r) - \rho_0$. In Al, where the effect should be most pronounced owing to its high valency and small r_c, the change was 0.5 eV with a largest R of 15 a.u. Taking the average of the two extrema will reduce the estimated error to 0.25 eV. We also used $R = 15$ a.u. in Li and Na. For r_c we used 1.83, 2.30, and 1.51 a.u. in Li, Na, and Al, respectively.

We end this section with a short note on the bound valence state in Na. The Kohn-Sham one-particle wave functions and energies are computational quantities without direct physical significance. Thus within the present theory the bound state has no relevance for excitation spectra. It merely contributes to the electron density and the total energy. However, the local density one-body exchange-correlation potential is rather similar to a local density approximation for the self-energy operator describing quasiparticles. Hence there is a possibility of having localized s-like

quasiparticle states showing up as peaks just below the satellite band. At least we expect an enhancement of the low-energy side of the satellite band due to an s resonance. The experiments by Hanson et al.[25] seem to support this conjecture.

B. Nonlinear effects

The largest valence-electron contribution $^s\Sigma_p$ to the core-electron self-energy,[5] is due to the polarization potential V_p, defined as the difference between the core function expectation value of the Hartree potential from the valence electrons V_H^v, with (*) and without (0) core hole(s)

$$V_p = \langle c | V_H^v | c \rangle_* - \langle c | V_H^v | c \rangle_0 \ . \tag{19}$$

The ΔSCF method offers an accurate way of estimating the nonlinear effects in $^s\Sigma_p$. Rewriting (2) as

$$\rho = \sum_i^{occ} n_i | \varphi_i |^2 \ , \tag{20}$$

we consider the nonphysical but nevertheless mathematically convenient procedure to solve the self-consistent equations (7)–(10) and (20) using nonintegral values for the occupation number n_c of the core state under consideration. The energy E_v [Eq. (14)] will then be a function of n_c and it is readily shown that

$$\frac{\partial E_v}{\partial n_c} = \epsilon_c - \epsilon_F \ , \tag{21}$$

where ϵ_c is the Kohn-Sham one electron energy relative to the bottom of the valence band. In the ΔSCF method the core quasiparticle energy E_c at threshold is taken as

$$E_c = E_v(n_c) - E_v(n_c - 1) \ , \tag{22}$$

or from Eq. (21)

$$E_c = \int_{n_c-1}^{n_c} \epsilon_c(n) \, dn - \epsilon_F \tag{23}$$

where n_c is the ground-state occupation number ($n_c = 6$ for an $L_{2,3}$ edge). Since ϵ_c is the expectation value with respect to the core function $| c \rangle$ of the left-hand side of Eq. (7), E_c contains the contribution $\int_{n_c-1}^{n_c} V_p(n) \, dn$ from the polarization potential, and we have[5]

$$^s\Sigma_p = \int_{n_c-1}^{n_c} V_p(n) \, dn \ . \tag{24}$$

By definition $V_p(n_c) = 0$, and since we have performed self-consistent calculations both for the ground state ($n = n_c$) and for states containing one and two core holes ($n = n_c - 1$ and $n = n_c - 2$), we know $V_p(n_c - 1)$ and $V_p(n_c - 2)$ from Eq. (19). We are thus able to do a quadratic interpolation for V_p:

$$V_p(n) = (n - n_c) [\tfrac{1}{2}(n - n_c + 1) V_p(n_c - 2)$$

$$-(n - n_c + 2) V_p(n_c - 1)] \ . \tag{25}$$

To test the accuracy of this interpolation we used the same interpolation for the eigenvalue $\epsilon_c(n)$ as a function of the core-state occupation number. Equation (23) then provides an independent way of obtaining the energy E_c which can be compared with using Eq. (22). An agreement within 0.5% was found in all cases showing third-order effects to be negligible. The close agreement also demonstrates the high over-all numerical accuracy achieved in our calculations.

Keeping only linear terms in Eq. (25),

$$V_p^L(n) = (n - n_c) [\tfrac{1}{2} V_p(n_c - 2) - 2 V_p(n_c - 1)] \ ,$$

we obtain the linear part $^s\Sigma_p^{(1)}$ of the polarization contribution to the self-energy from Eq. (24)

$$^s\Sigma_p^{(1)} = V_p(n_c - 1) - \tfrac{1}{4} V_p(n_c - 2) \ . \tag{26}$$

This expression is equivalent to the one used by Hedin[4] provided V_p is taken from electron-gas data. However, using the full expression (25) for V_p in Eq. (24) we obtain an additional contribution $\Sigma_p^{(2)}$ to Σ_p

$$^s\Sigma_p^{(2)} = \tfrac{1}{8} V_p(n_c - 2) - \tfrac{1}{3} V_p(n_c - 1) \ , \tag{27}$$

$$^s\Sigma_p = {}^s\Sigma_p^{(1)} + {}^s\Sigma_p^{(2)} \ . \tag{28}$$

For the doubly ionized levels the polarization contribution to the self-energy ($^d\Sigma_p$) is easily obtained by replacing n_c with $n_c - 1$ in the limits of Eq. (24) and subtracting $V_p(n_c - 1)$. The different Σ_p's are given in Table III showing the strong non-linear effects that appear especially for the doubly ionized levels.

C. Edge singularities

Using a spherical model Nozières and De Dominicis[11] (ND) showed that the shape of x-ray emission or absorption spectrum was given by

$$I(\omega) = \sum_{l=0}^{\infty} A_l(\omega) \left(\frac{\omega_0}{\omega - \omega_T} \right) \alpha_l \ , \tag{29}$$

close to the threshold energy ω_T. Here ω_0 is some cutoff frequency of the order of ϵ_F and $A_l(\omega)$ are the ordinary one-body golden-rule transition amplitudes which in a spherical model are given by

$$A_l(\omega) = \tfrac{4}{3} (2l + 1) \begin{pmatrix} l_c & l & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 M_{cl}^2(k_c) k_c^{-1} B(\omega - \omega_T) \ , \tag{30}$$

where $k_c = [2(\omega - \omega_T + \epsilon_F)]^{1/2}$, l_c is the l quantum number of the relevant core hole, $B(\omega)$ is $\Theta(\omega)$ for absorption and $\Theta(-\omega)\Theta(\omega + \epsilon_F)$ for emission, $\Theta(\omega)$ being the unit step function, and

$$M_{cl}(k) = \int_0^{\infty} P_c(r) P_{kl}(r) r \, dr \ . \tag{31}$$

The factor after $2l + 1$ is the square of the Wigner

"3j" symbol, P_c and P_{kl} are the core and valence radial wave functions behaving like r^{l_c+1} and r^{l+1} for small r, and the P_{kl}'s are normalized according to

$$\int_0^{\infty} P_{kl}(r) P_{k'l}(r) \, dr = \delta(k - k') \ .$$

Consider an interacting electron gas subject to an external spherical potential $W(r)$ (the potential from a core hole). The screened version of this potential is $W^s(r)$. Nozières and De Dominicis showed that the shape of the x-ray absorption spectrum close to the threshold could be obtained by considering a noninteracting gas into which suddenly the potential $W^s(r)$ is introduced. They also showed that the exponents α_l in Eq. (29) are given by

$$\alpha_l = \frac{2}{\pi} \delta_l - \frac{2}{\pi^2} \sum_{l=0}^{\infty} (2l + 1) \delta_l^2 \ , \tag{32}$$

where δ_l are the Fermi-level phase shifts of the self-consistently screened potential W^s. In the Appendix we have made a minor modification of the ND theory to show that, in our case, the relevant phase shifts to be used in Eq. (32) are the difference between the Fermi-level phase shifts for our self-consistent potentials with and without core hole. It has been demonstrated by Hopfield[29] that the details of the edge is connected to the transfer of charge of different angular momentum symmetry involved in the screening of the core hole. This charge transfer is described by the difference in the phase shifts and not by the phase shifts of the difference potential. Note that the latter phase shifts do not obey the sum rule while the difference phase shifts do, as do the phase shifts of a screened potential. We also note that the nonphysical difference potential most certainly possesses a bound state.[30]

Our results for the difference phase shifts

TABLE III. Linear and nonlinear parts, $\Sigma_p^{(1)}$ and $\Sigma_p^{(2)}$, of the polarization contribution to the self-energy of core levels (nl), in the ground state $(^s\Sigma)$, and in the "ground state" with a core hole (h) present $(^d\Sigma)$, for Li, Na, and Al. V_p is the difference in valence Hartree potentials for the core levels (nl) with and without core hole. $^d\Sigma_p^{(1)} = {}^s\Sigma_p^{(1)}$, $^d\Sigma_p^{(2)} = 4\,{}^s\Sigma_p^{(2)}$. Energies in eV.

	nl	h	$^s\Sigma_p^{(1)}$	$^s\Sigma_p^{(2)}$	V_p	$^d\Sigma_p^{(1)}$	$^d\Sigma_p^{(2)}$
Li	$1s$	$1s$	6.48	0.93	15.75	6.48	3.74
Na	$1s$	$2p$	5.55	0.46	12.48	5.55	1.84
Na	$2s$	$2p$	5.23	0.38	11.60	5.23	1.52
Na	$2p$	$2p$	5.23	0.39	11.64	5.23	1.57
Al	$1s$	$2p$	8.90	0.52	19.35	8.90	2.06
Al	$2s$	$2p$	8.12	0.42	17.50	8.12	1.67
Al	$2p$	$2p$	8.18	0.44	17.68	8.18	1.75

TABLE IV. Difference phase shifts relevant to the Nozières–De Dominicis model. α_l is the edge exponent

$$\alpha_l = (2/\pi)\Delta\delta_l - (2/\pi^2) \sum_{l=0}^{N} (2l+1) \ (\Delta\delta_l)^2$$

$N+1$ is the number of l values used in the calculation, and F_N is the difference in the Friedel sum

$$F_N = (2/\pi) \sum_{l=0}^{N} (2l+1) \ \Delta\delta_l \ .$$

The d/s ratio refers to the Fermi level of the indicated final state.

	$\Delta\delta_0$	$\Delta\delta_1$	$\Delta\delta_2$	α_0	α_1	α_2	F_N	N	d/s ratio
Li $1s^1 \to 1s^2$	0.67	0.33	-0.02	0.27	0.05	-0.17	1.0004	7	$\cdots$
Li $1s^0 \to 1s^1$	0.37	0.46	-0.04	0.08	0.13	-0.18	1.0004	7	$\cdots$
Na $2p^5 \to 2p^6$	0.90	0.23	0.00	0.38	-0.05	-0.20	0.9999	7	0.11
Na $2p^4 \to 2p^5$	0.53	0.37	-0.01	0.20	0.10	-0.15	0.9993	7	0.11
Al $1s^1 \to 1s^2$	0.32	0.47	-0.01	0.05	0.14	-0.16	1.00003	13	$\cdots$
Al $2p^5 \to 2p^6$	0.30	0.43	0.01	0.06	0.14	-0.12	1.00001	13	0.52
Al $2p^4 \to 2p^5$	0.19	0.46	0.00	-0.01	0.16	-0.13	1.00005	13	0.87

$\Delta\delta_l(\epsilon_F)$ and the corresponding exponents α_l are shown in Table IV. Judging from the variation of the phase shifts with the numerical parameters and with the "environmental" parameter r_c discussed in Sec. III A we believe that the absolute accuracy of the exponents α_l to be 0.03. Because of the "$3j$" symbol in Eq. (30) only valence electrons of p symmetry will contribute to the shape of the edge in the case of an s hole, e.g., the K edge in Li. For the $L_{2,3}$ edges in Na and Al both s and d valence electrons contribute, and we give their relative contributions to the amplitudes $A_l(\omega_T)$ in Table IV. It is seen that the d contribution in Al is five times smaller than that expected by Mahan.[7]

In Li we obtain $\alpha_1 = 0.05$ for the relevant exponent. Taking different broadening effects into account the resulting enhancement should not be experimentally observable. Thus the effect of final-state interactions of the ND type are negligible in Li and does not explain the broad structure found experimentally. However, the electron-energy-loss experiments by Gibbons et al.[31] give rise to serious doubts concerning the validity of the present version of the ND theory. These experiments involve a Coulomb matrix element and since the momentum transfer can be varied the valence electrons of s symmetry will also contribute to the shape of the edge.[32] Since we obtain $\alpha_0 = 0.27$ the ND theory predicts a sharpening of the Li K edge with increasing momentum transfer, while the experiment by Gibbons et al. show no change of the edge. Gibbons et al. actually claim that their experiment is not compatible with the ND theory unless the phase shift for the s wave is less than 0.5 ($\delta_0 < 0.5$). We obtain $\delta_0 = 0.67$ but we note that the limit 0.5 given by Gibbon et al. is sensitive to the rather unknown cutoff frequency

ω_0 and the likewise unknown ratio of the contributions from s and p waves.

We want to stress our belief that since the ND theory is based on a spherical model the only relevant phase shifts to be put in the formula (29) are the phase shifts $\Delta\delta_l$ of Table IV. If these lead to contradictions with experimental results, it is rather the present form of the ND theory that has to be revised like the crude choice of potential and the spherical approximation. Since the ND theory concerns quasiparticle states, one might argue that we should have used the self-energy operator instead of the Kohn-Sham potential to get out differences in Fermi-level phase shifts. At the Fermi level, however, the difference between the two potentials is small enough not to affect our basic conclusion.

In Na we obtain $\alpha_0 = 0.38$, thus predicting a noticeable enhancement which is also found experimentally. In Al we obtain $\alpha_0 \sim 0.06$ which means a negligible ND effect. It is generally believed that there is an enhancement in Al but it is also known that there is a peak at the Fermi level in the density of states.[33] This peak is easily confused with a many-body effect. Neddermeyer[34] fitted his experimental K and $L_{2,3}$ spectra for Al to the formula (29) and obtained $\alpha_1 = 0.02 \pm 0.07$ and $\alpha_0 = 0.16 \pm 0.06$ compared to $\alpha_1 = 0.14$ and $\alpha_0 = 0.06$ in Table IV. Dow and Sonntag[8] fitted the $L_{2,3}$ absorption data on Na, Mg, and Al by Kunz[35] et al. to a broadened form of Eq. (29) and obtained an empirical rule obeyed by the α_0 exponents, $\alpha_0 = 0.068r_s$. The rule implies $\alpha_0 = 0.14$, 0.22, and 0.27 for Al, Li, and Na compared to our $\alpha_0 = 0.06$, 0.27, and 0.38 for the same materials. Our agreement with experimental results is relatively poor thus suggesting that either the Mahan[36] edge shape [Eq. (29)] or the ND formula [Eq. (32)]—for

the exponents has to be abandoned in accordance with Dow's[8-10] conclusions. It should be kept in mind that strong matrix element effects and unknown broadening effects make it difficult to extract exponents from experimental spectra. The strongest experimental support for a ND-type many-body effect is found in Na, and in this case the theory predicts a noticeable effect. Thus, in order to resolve the present controversy an energy-loss experiment performed on Na would be most helpful.

Final-state interactions of the ND type are also responsible for the asymmetry of x-ray photoemission (XPS) core lines.[37] According to Nozières and De Dominicis[11] the core-hole spectral function $A_c(\omega)$ is proportional to

$$A_c(\omega) \propto [(\omega - \omega_T)^2 + \gamma^2]^{(\alpha-1)/2} \tag{33}$$

for ω close to ω_T. Here

$$\alpha = \frac{2}{\pi^2} \sum_{l=0}^{\infty} (2l+1)\delta_l^2 \tag{34}$$

and γ represents the inverse lifetime of the core hole. Thus by fitting the form (33) to the experimental XPS core spectra one can extract α and get an independent check on the quantitative validity of the ND theory. We believe this to be a more reliable test of the ND theory for the following three reasons: (i) Contrary to the XPS case, the extraction of exponents from an x-ray emission or absorption experiment is strongly influenced by band-structure effects also at threshold. (ii) Mahan[7] has clearly demonstrated that many-body effects affect the whole x-ray spectrum and that a strict power law, shown by ND to be asymptotically valid at threshold, only applies very close to the edge. Therefore a power-law fitting to the experimental x-ray spectra might be dubious. To our knowledge no attempt has been made to fit the spectra with the formula recently put forward by Mahan[7] and which he claims to be valid also away from the edge (when Mahan compared his formula to the experimental results the exponents were not treated as fitting parameters). (iii) New calculations in Lund[38] of the core-hole spectral function shows that the power law (33) is applicable

TABLE V. Singularity exponents for x-ray emission or absorption (α_0, α_1) and for x-ray photoemission (α).

	α_0[a]	α_1[a]	α[a]	α[b]	α[c]
Li K	0.27	0.05	0.16	$\cdots$	0.18
Na $L_{2,3}$	0.38	-0.05	0.20	0.19	$\cdots$
Al $L_{2,3}$	0.06	0.14	0.13	0.12	0.16

[a]This work.
[b]Citrin and Wertheim, Ref. 39.
[c]Ley et al., Ref. 40.

also quite far away from the maximum of the core peak.

Recently Citrin and Wertheim[39] made a careful extraction of the exponents (α) from their XPS spectra on Na, Mg, and Al and in Table V we compare their exponents with our calculated α's. The agreement is gratifying and strongly supports the ND theory. Table V also shows exponents extracted by Ley et al.[40] from their XPS data on Li, Mg, and Al. For Mg Ley et al. obtain the same value as Citrin and Wertheim but the corresponding numbers for Al differ markedly. We prefer the result by Citrin since this result is obtained by fitting the whole peak with the formula (33) instead of just using the asymmetry at half maximum as is done by Ley et al. According to Citrin et al. it is actually the tail of the peak that determines α which seems reasonable to judge from the results by Minnhagen.[38]

It is generally believed[9] that the potentials from screened core holes in different shells, are very similar as far as deep core holes are concerned. Our calculation of the K threshold in Al was primarily performed to test this assumption. As can be seen from the phase shifts in Table IV the potential from the $1s$ hole is indeed very similar to the potential from $2p$ hole.

D. Ground state and matrix elements

In the previous sections we have demonstrated that core excitations in simpler metals are very well described by the SSM. These excitations involve the difference between ground and excited states or between excited states. However, it turns out that ground-state properties are poorly described by the SSM. This was to be expected from the way it was constructed, and the model was not intended to do a good job on the ground state except in the vicinity of the central nucleus. In the SSM the valence charge density on the different nuclei will tend to the homogeneous density ρ_0, with increasing distance from the central nucleus, whereas the electron density should be the same on all nuclei and two orders of magnitude larger than ρ_0. In a band calculation the periodic boundary condition will automatically guarantee charge neutrality within each unit cell. In the SSM no such mechanism exists and it turned out that there was too little charge within the Wigner-Seitz sphere in Li and Na, but a correct amount in Al. In Table VI we show the r_s value, the Wigner-Seitz radius r_{ws}, the radius r_0 of a sphere containing the number of valence electron appropriate to the unit cell, and the number Q_{ws} of electrons contained within r_{ws} for the SSM ground states of Li, Na, and Al.

It is interesting to investigate how well different structures in the density of states of a band cal-

TABLE VI. r_s values, Wigner-Seitz radius r_{WS}, and the radius r_0 containing the number of electrons appropriate to the unit cell. Q_{WS} is the number of electrons within r_{WS} and Z_v is the valency. Atomic units.

	r_s	r_{WS}	r_0	Z_v	Q_{WS}
Li	3.27	3.27	3.38	1	0.89
Na	4.00	4.00	4.11	1	0.92
Al	2.07	2.99	2.99	3	3.01

culation are reproduced by the SSM. Owing to periodicity the local density of states, defined as an average over the unit cell of the spectral function, is the same as the global density of states of a band calculation. Since the SSM is equivalent to a local disturbance in an electron gas the global density of states is always a square-root law in the SSM. It is rather the local density of states that should be compared to that of a band calculation. Since there is an arbitrariness in the definition of the local density of states we have decided to look directly at the one-electron theory of x-ray emission. In the SSM this is given by $A_0(\omega)$ $+A_2(\omega)$ for a $2p$ core hole. The $A_l(\omega)$'s are defined in Eq. (30) with c replaced by $2p$.

We have plotted the quantity $A_0 + A_2$ in Fig. 1 both for the ground state and for the state with a hole in the $2p$ shell. The ground-state curve can be compared with the corresponding curve by Smrcka[33] obtained from a full band calculation. The energy scale of the SSM curve has to be multiplied by a factor of 2 in order for this curve to have any resemblance with the Smrcka result. The change in the SSM curve when we go from the

ground state to the state with one $2p$ core hole is essentially a further 30% compression of the energy scale. The curve by Smrcka is obtained in the ground state without core hole while the emission starts from the state with the core hole present, and should be described accordingly. However, the close agreement between Smrcka's result and the experimental spectrum indicates that the effect of final state interactions is small in contrast to the SSM result.

On the other hand the satellite bands from doubly ionized core levels show strong deviations from the shape of the main band.[25] The oscillator strength of s character is shifted to lower energies in the satellites as predicted by the SSM. Our present version of the SSM is thus only able to give gross trends for ground-state properties and further investigations are needed.

IV. SUMMARY

We have developed a "spherical solid" model (SSM) to treat very localized excitations in metals. We have tested the model in a calculation of the position of x-ray edges and their associated satellites due to double ionization in Li, Na, and Al. The agreement with experimental energies was of the order of 0.5 eV for singly ionized levels, and 1 eV for doubly ionized levels. For the K edge in Al our result was 3 eV off but it was argued that the discrepancy could easily be removed by an improved treatment of atomic relaxation effects. Our model indicates that strong s resonances should enhance the low energy side of the satellite bands. This seems to be in accord with experimental findings[25] (Sec. III A).

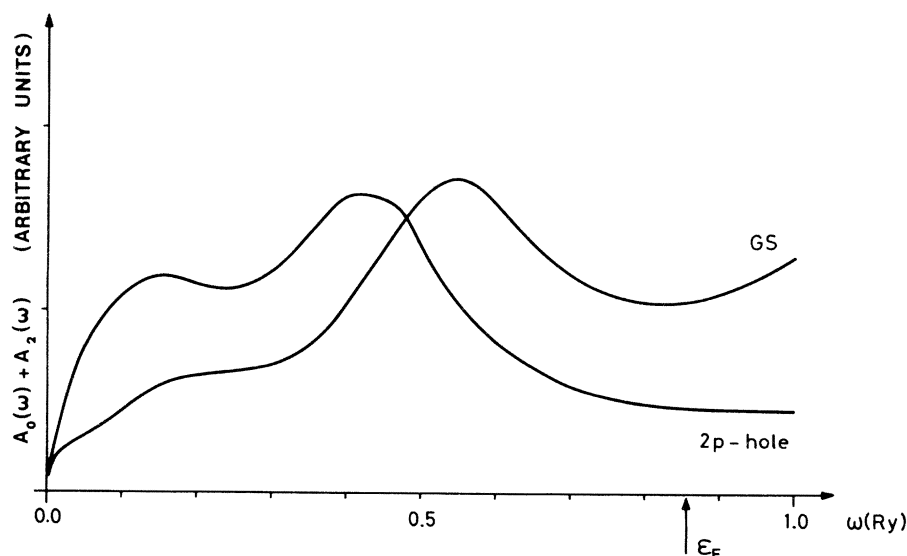We have discussed the SSM from the standpoint

FIG. 1. Results for soft-x-ray emission intensities calculated in the spherical solid model in the ground state (GS), and with a $2p$ hole in aluminum.

of self-energy approximations and reached the conclusion that in Na and Al 0.5 eV is an upper bound to the accuracy that can be achieved for a singly ionized core level in the linear so-called GW approximation,[3] while in Li the appropriate upper bound is as large as 1 eV. Nonlinear effects are thus important already for singly ionized levels and for multiply ionized levels they are absolutely essential (Sec. III B).

The SSM enables us to calculate the phase shifts describing the scattering of a Fermi-level electron off a core-hole potential. In a spherical model Nozières and De Dominicis[11] (ND) obtained expressions relating these phase shifts to the shapes of the x-ray absorption and emission edges and to the x-ray photoemission (XPS) line shapes. The shapes of the edges obtained with our phase shifts are sufficiently different from the experimental results[8,34] to question the validity of the present form of the ND theory. This is true in particular for the case of Li where the result from energy-loss experiments[31,32] seem incompatible with the use of SSM phase shifts in the ND theory. On the other hand the ND theory is strongly supported by the fact that our XPS line shapes agree extraordinarily well with recent photoemission experiments[39] on Na and Al. We argue that strong and unknown effects of broadening, matrix elements, and band structure make it difficult to extract phase shifts from the x-ray absorption and emission spectra. The phase shifts extracted from the XPS experiments should thus be more reliable (Sec. III C). We dare not, however, draw any definite conclusion concerning the validity of the ND theory until the experimental situation has become more clear.

The SSM gives a rather poor description of ground-state properties. For example, the SSM one-particle description of soft x-ray emission does not agree with the result from a band-structure calculation.[33] The reason is that in the SSM the charge on the nuclei surrounding the central atom is spread out on spherical shells and the back scattering from these shells has only a weak resemblance to the scattering in a real lattice. However, the scattering off the central atom is probably very similar to the scattering off a single atom in a real crystal and accordingly the SSM should be applicable in cases with weak multiple scattering (Sec. III D).

The principle we have used for constructing our *ab initio* spherically averaged potential, is not the only conceivable one, and it may be possible to make a more optimal choice that results in better SSM predictions for the one-particle spectral shapes. We feel on the other hand that the results obtained here are very encouraging from further SSM investigations.

APPENDIX

In this appendix we establish the connection between the ND model and the SSM phase shifts. Consider two model Hamiltonians of the ND type[11]

$$H_1 = \sum_k \epsilon_k c_k^\dagger c_k + \sum_{kk'} V_{kk'}^{(1)} c_k^\dagger c_{k'} \, , \tag{A1}$$

$$H_2 = \sum_k \epsilon_k c_k^\dagger c_k + \sum_{kk'} V_{kk'}^{(2)} c_k^\dagger c_{k'} \, , \tag{A2}$$

describing the low-lying particle-hole excitations in a metal in its ground state (H_1) and when one particular core-level is empty (H_2).

The electron operators $\{c_k\}$ refer to the plane wave representation and ϵ_k is a free-electron energy. In the spirit of the ND theory[11] we consider the scattering potentials to be spherically symmetric, and furthermore we neglect the difference between the self-energy and the Kohn-Sham ground-state potential. With these approximations the scattering potentials V_1 and V_2 are reduced to the self-consistent potentials obtained by the SSM. The original ND model was characterized by having $V^{(1)} \equiv 0$. However, if $\{\phi_n^{(1)}\}$ are the eigenfunctions of H_1 and $\{a_n\}$ are the corresponding electron annihilation operators, we can write

$$H_1 = \sum_n \epsilon_n a_n^\dagger a_n \, , \tag{A3}$$

$$H_2 = \sum_n \epsilon_n a_n^\dagger a_n + \sum_{nn'} V_{nn'} a_n^\dagger a_n \, , \tag{A4}$$

and the model described by the Hamiltonians H_1 and H_2 are in fact equivalent to the original ND model (for simplicity we only consider s waves).

A solution for the x-ray edge shape within the ND model has so far only been obtained for separable potentials

$$V_{nn'} = V_0 U(\epsilon_n) U(\epsilon_{n'}) \, , \tag{A5}$$

and the phase-shift parameter $\delta(\epsilon)$, which enters in the ND expression for the edge exponent, is given by

$$\tan \delta(\epsilon) = \frac{\pi V_0 U^2(\epsilon) \nu(\epsilon)}{1 - V_0 y(\epsilon)} \, , \tag{A6}$$

$$y(\epsilon) = \int d\epsilon' \, \nu(\epsilon') U^2(\epsilon') \frac{P}{\epsilon' - \epsilon} \, , \tag{A7}$$

where $\nu(\epsilon)$ is the density of (s) states and P denotes the principal part of the integral.

The SSM gives the phase shifts $\delta^{(1)}$ and $\delta^{(2)}$ of

the potentials $V^{(1)}$ and $V^{(2)}$. Thus, in order to use the difference $\delta^{(2)} - \delta^{(1)}$ in the ND formula for the edge exponent [Eq. (32)] we must show that

$$\delta = \delta^{(2)} - \delta^{(1)} . \tag{A8}$$

This relation does only make sense when the potential $V_{nn'}$ in Eq. (A4) is separable, and the application of the ND expression [Eq. (32)] to more general potentials, although widely used, is only an extrapolation of unproven validity.

In order to prove the relation (A8) we express the eigenfunctions $\{\phi_n^{(2)}\}$ of H_2 in terms of $\{\phi_n^{(1)}\}$

$$\phi_n^{(2)} = \sum_{n'} A(\epsilon_n, \epsilon_{n'}) \phi_{n'}^{(1)} . \tag{A9}$$

Requiring this transformation to diagonalize H_2 and going over to continuous variables ϵ and ϵ' we obtain a separable integral equation for $A(\epsilon, \epsilon')$, due to the separability of the potential $V_{nn'}$ [Eq. (A5)]

$$(\epsilon' - \epsilon) A(\epsilon, \epsilon')$$

$$= V_0 U(\epsilon') \int A(\epsilon, \epsilon'') U(\epsilon'') \nu(\epsilon'') d\epsilon'' . \tag{A10}$$

The solution of this integral equation is readily found to be

$$A(\epsilon, \epsilon')$$

$$= \left(V_0 \frac{U(\epsilon) U(\epsilon') \nu(\epsilon)}{1 - V_0 y(\epsilon)} \frac{P}{\epsilon' - \epsilon} + \delta(\epsilon - \epsilon') \right) D(\epsilon) . \tag{A11}$$

Here $y(\epsilon)$ is given by Eq. (A7), and $D(\epsilon)$ is determined by the unitarity of the transformation $A(\epsilon, \epsilon')$, i.e.,

$$\int A(\epsilon, \epsilon'') A(\epsilon', \epsilon'') \nu(\epsilon'') d\epsilon'' = \frac{1}{\nu(\epsilon)} \delta(\epsilon - \epsilon') . \tag{A12}$$

Using the identity

$$\frac{P}{\epsilon'' - \epsilon} \frac{P}{\epsilon'' - \epsilon'} = \frac{P}{\epsilon - \epsilon'} \left(\frac{P}{\epsilon'' - \epsilon} - \frac{P}{\epsilon'' - \epsilon'} \right)$$

$$+ \pi^2 \delta(\epsilon - \epsilon') \delta(\epsilon - \epsilon'') , \tag{A13}$$

and the Eqs. (A11) and (A12), we obtain the final expression for the transformation $A(\epsilon, \epsilon')$

$$A(\epsilon, \epsilon') = \frac{1}{\nu(\epsilon)} \left(\cos\delta(\epsilon) \delta(\epsilon - \epsilon') \right.$$

$$\left. + \frac{\sin\delta(\epsilon)}{\pi} \frac{U(\epsilon')}{U(\epsilon)} \frac{1}{\epsilon' - \epsilon} \right) . \tag{A14}$$

The large r asymptotic behavior of the continuum function $\phi_\epsilon^{(2)}(r)$ can now be expressed in terms of $\delta^{(1)}(\epsilon)$, $\delta(\epsilon)$, $k = \sqrt{\epsilon}$,

$$\phi_\epsilon^{(2)}(r) \sim \cos\delta(\epsilon) \sin[kr + \delta^{(1)}(\epsilon)] + \sin\delta(\epsilon) \frac{1}{\pi}$$

$$\times \int \frac{U(\epsilon')}{U(\epsilon)} \frac{\nu(\epsilon')}{\nu(\epsilon)} \sin[k'r + \delta^{(1)}(\epsilon')] \frac{P}{\epsilon' - \epsilon} d\epsilon'$$

$$\tag{A15}$$

The asymptotic limit of the last term in Eq. (A15) is simply $\sin\delta(\epsilon) \cos[kr + \delta^{(1)}(\epsilon)]$,[43] and consequently the asymptotic form of $\phi_\epsilon^{(2)}(r)$ is $\phi^{(2)}(r)$ $\sim \sin[kr + \delta^{(1)}(\epsilon) + \delta(\epsilon)]$ which proves Eq. (A8).

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†The major results from this work were part of the authors' dissertations submitted in partial fulfillment of the requirements for a Ph. D. degree.

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