

Lack of mirror symmetry between x-ray absorption and emission edges of simple metals

P. A. Bruhwiler,* Peteris Livins,[†] and S. E. Schnatterly

Jesse Beams Laboratory of Physics, University of Virginia, Charlottesville, Virginia 22903

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We have calculated core emission and absorption spectra for a free-electron metal, using a determinantal method. The results indicate that the Mahan-Nozières-De Dominicis model is accurate near threshold to the extent testable with experimental data. Experimental data however, analyzed using the energy range justified above, indicate that the expected mirror symmetry rarely exists. Furthermore, Na core photoemission line shapes are incompatible with absorption and emission. We suggest a possible explanation for these discrepancies.

Our present understanding of the threshold shapes of soft x-ray core spectra is based on the work twenty years ago by Mahan¹ and Nozières and De Dominicis² (MND). Much effort has been expended since to quantitatively compare the MND model with experiment.³ This problem remains an important subject of study in part because it is the only example in physics of a spectroscopically observable infrared divergence. The MND expression for the spectral intensity at an x-ray-absorption threshold is

$$I(E) \propto \sum_{l=0}^{\infty} A_l(E) \left(\frac{\xi}{E - E_T} \right) \alpha_l \Theta(E - E_T), \quad (1)$$

where the $A_l(E)$ are the dipole transition matrix elements, ξ is a scaling parameter of the order of the Fermi energy (E_F), and E_T is the threshold energy. α_l is given by

$$\alpha_l \equiv \frac{2\delta_l}{\pi} - \alpha \quad \text{with} \quad \alpha \equiv 2 \sum_{l=0}^{\infty} (2l+1) \left(\frac{\delta_l}{\pi} \right)^2. \quad (2)$$

The δ_l are the phase shift changes at E_F for single-particle conduction states of angular momentum l , evaluated using the initial and final potentials. Many workers have calculated the phase shifts and thus the exponents, using a screened core potential; the results vary widely and are summarized in Ref. 4. Since the δ_l are obtained by taking the differences between the phase shifts before and after the optical event, creating and annihilating the core hole should yield equivalent line shapes. That is, the singularities measured in soft x-ray absorption (SXA) and emission (SXE) are expected to be the same. Only for Al do p -core thresholds data indicate such behavior;⁴ Mg (Ref. 4), Na (Ref. 5), and K, Rb, and Cs (Refs. 6 and 7) all exhibit p -core absorption edges that are significantly more sharply peaked than the corresponding emission edges. One possible explanation for this is that the data are being analyzed too far from threshold, so that the asymptotic result [Eq. (1)] is not appropriate. Another possibility, suggested by the results of several groups,⁸⁻¹⁰ is that the nature of the potentials in emission and absorption is not yet fully understood.

We have calculated absorption and emission spectra using a determinantal method,¹¹ which should be accurate both near and away from threshold for as few as 80 states.¹² The work of Ohtaka and Tanabe¹³ was incorporated to obtain the absorption spectrum; both spectra

were generated using 150 s waves, and first-order shake-up¹¹ was included. Inclusion of first-order shakeup exhausted the emission sum rule^{12,14} by 99.9%. We used the exponential form of von Barth and Grossmann¹² to approximate the dipole-matrix elements of Na. E_F was taken to be 3.1 eV and we chose a square well to simulate the effect of the core vacancy, with a radius equal to the Thomas-Fermi screening length ($\lambda_s = 0.67 \text{ \AA}$) and a depth such that the phase shifts produced $\alpha_0 \approx 0.22$, the experimentally observed value reported below. Odd- l components of the conduction-electron wave function are forbidden by the dipole selection rule, and the $l=2$ contributions can be neglected^{4,15} so that α_0 should accurately characterize the spectra. We include the appropriate density of states (DOS) by dividing the strength of each line, one per occupied state, by the energy spacing of the states at that point.

In Fig. 1 we show emission and absorption spectra calculated as described above. As is evident, the calculated

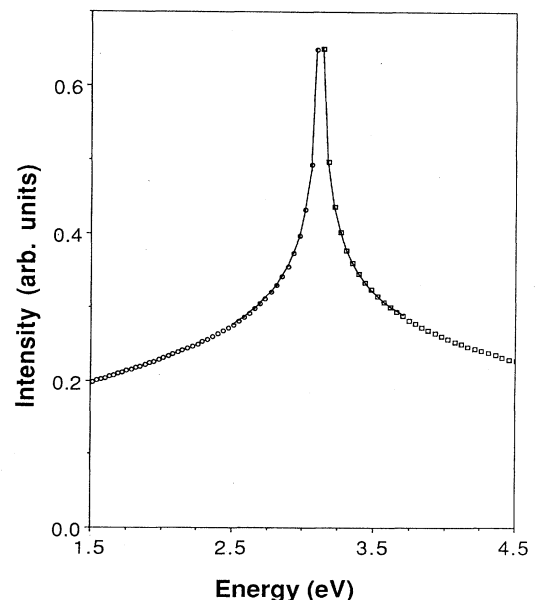


FIG. 1. Calculated emission and absorption spectra appropriate for Na, with power-law fit described in the text.

spectra are peaked quite similarly. According to a reasonable extension¹² of the final-state rule^{11,12} (FSR), the spectra are equivalent to the transition DOS (TDOS) of the final state multiplied by the power law defined in Eq. (1). By dividing each spectrum by the FSR TDOS and taking the logarithm, we obtain a function whose slope at a given energy is equivalent to α_0 at that point. We plot $\alpha_0(E)$ in Fig. 2 using the absolute value of the separation from E_F as the abscissa. It is apparent that $\alpha_0(E)$ in emission is fairly constant near 0.245 over a wide range, and in absorption is accurately a linear function, $[\alpha_0(E)]_{\text{abs}} \approx 0.195 - 0.04E$. The lines through the points in Fig. 1 use these two forms for $\alpha_0(E)$ in Eq. (1).

We have repeated the calculations above with Fermi energies of 1 and 10 eV. A criterion for evaluating a determinantal calculation in terms of the MND model was developed by von Barth and Grossmann.¹² They proposed¹² evaluating $C(E) = I(E)/J(E)E^{-\alpha_0}$, where $I(E)$ is the calculated intensity and $J(E)$ the FSR TDOS. If $C(E)$ is flat, or nearly flat, then the MND model can be said to represent the spectral shape well.

We have evaluated $C(E)$ for all three above values of E_F and find that it is flat or nearly flat in each case. The log graphs appear to be more sensitive to the details of the calculation; however, when $\alpha_0(E)$ has a significant slope $C(E)$ deviates from flatness in the expected manner. To explore the reliability of $C(E)$ as a criterion for testing the MND model we fit the spectra of Fig. 1 over the same ranges indicated there, using an energy independent α_0 . The fits, which passed through all data points within assigned uncertainties of 1% yielded $(\alpha_0)_{\text{SXE}} = 0.233$ and $(\alpha_0)_{\text{SXA}} = 0.217$, providing striking confirmation of the usefulness of $C(E)$ and the validity of the MND model over this energy range. With E_F equal to 3 and 10 eV, the results for the log graphs are very similar. For absorption we find an intercept close to but smaller than the expected value of α_0 , with slopes in the range of -0.04 to -0.10 eV⁻¹. For emission, the intercept again remains as given above with slopes in the range 0 to 0.1 eV⁻¹. With $E_F = 1$ eV, the exponents change more rapidly with energy.

The slopes we find for $\alpha_0(E)$ are opposite in sign to those predicted by Kita,¹⁶ who studied intrinsic aspects of the dynamical problem. The variations we observe are probably not inherent to the dynamical problem since we find that we can change the slopes by altering the form of the dipole-matrix element, e.g., between that used in Ref. 12 and that used in Ref. 17. These small slopes of $\alpha_0(E)$

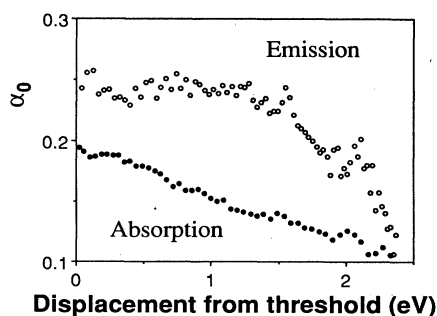


FIG. 2. Energy dependence of α_0 in the spectra of Fig. 1.

are not observable in experimental spectra, as we have shown above. They do give us one measure of the uncertainty in values of α_0 extracted from data.

An interesting aspect of the above results is that the two intercept values of α_0 , 0.195 and 0.245, differ from the expected value of 0.22 but are centered about that value. Our results are consistent with this behavior, being independent of the value of E_F the form of the dipole-matrix element, and the energy spacing of the states. It appears from these results that this difference is inherent to the problem and is caused by the asymmetry between occupied and empty states.¹¹

We have also analyzed¹⁸ experimental spectra using the same energy range indicated in Fig. 1 to determine α_0 from the data.^{19,20} For Na, the slope of the FSR TDOS (Refs. 4 and 21) plays only a small role in determining α_0 with our line-shape analysis.^{4,18,19} We have evaluated¹⁸ the asymmetric broadening due to partial phonon relaxation^{22,23} and find that it also fails to account for the gentler sloping of the Na $L_{2,3}$ SXE threshold, since the broadening function is less than 0.15-eV wide and resembles a Gaussian in both shape and broadening effect.^{18,24} The values we obtain are $(\alpha_0)_{\text{SXA}} = 0.22 \pm 0.02$ and $(\alpha_0)_{\text{SXE}} = 0.15 \pm 0.02$, which are consistent with those of previous analyses^{5,19,25} if the slight TDOS contribution is accounted for.¹⁸ Though Citrin, Wertheim, and Schluter⁴ find $(\alpha_0)_{\text{SXA}} = 0.38$, we feel that this discrepancy is primarily due to the different fitting criteria used, and will discuss this point further elsewhere.¹⁸ Our comparison of data with theory confirms what seems apparent by casual inspection, which is while the MND model accurately describes both experiments, different parameters are needed for absorption and emission. The only way we can force the two exponents to be equal is to assume TDOS slopes in emission and absorption add up to about -0.3 eV⁻¹, which disagrees with calculated values for Na.¹⁸ Furthermore, this explanation is unlikely to work at all for the heavier alkali metals which undoubtedly have positive s -wave slopes at E_F .

To explain a difference between absorption and emission using the present asymptotic model requires a change in the potential near the core between the two events. Indeed, such a change can occur due to phonon coupling. The absorption transition takes place with the nearby ions in their ground-state equilibrium positions. However, the emission transition usually occurs after the nearby ions have relaxed to new positions in the presence of the core potential. Thus the potential that is switched off in the emission transition will usually be different from that switched on in the absorption transition. We have estimated the effect of the lattice relaxation on α_0 using a model described elsewhere,²⁴ and find that it induces a change in α_0 of 0.03 so that the asymmetry in the determinantal result is approximately compensated. Thus we find no explanation for the experimentally observed lack of mirror symmetry between absorption and emission spectra of simple metals when all known effects are accounted for.

The MND model can be applied to x-ray photoemission (XPS) core line shapes as well,²⁶ for which the intensity near threshold should diverge as $1/E^{1-\alpha}$. It is therefore

possible to extract α [Eq. (2)] from these data. Citrin, Wertheim, and Baer²⁷ carried out an extensive analysis of XPS data from several metals and found that this power law described the data up to a range of $E_F/2$ away from threshold.

In order to remove as far as possible uncertainties in the peaking parameters determined from Na XPS spectra, we have investigated the influence of a previously unexamined effect, the surface core-level binding-energy shift (SCS), which is²⁸ 0.2 eV to higher binding energy in Na. Since the Na XPS spectra²⁷ available to date are expected²⁸ to have surface contributions of 15% ($2p$, $2s$) to 48% ($1s$), it is important to determine the SCS influence on the value of α extracted from data. We have used the algorithm of Kammerer *et al.*²⁸ to model the surface component, but keeping the spin-orbit splitting at 0.17 eV, and find $\alpha \approx 0.22$, near the previously determined value of 0.20.

If the MND model as stated in Eqs. (1) and (2) is accurate, a common set of phase shifts δ_l exist which yield $\alpha = 0.22$ and $\alpha_0 = 0.22$ when inserted in Eqs. (2). The Friedel sum rule $\sum (2l+1)\delta_l = \pi/2$ is a necessary constraint on the phase shifts,²⁹ and has been translated into exponent compatibility relations.^{4,19} If one assumes $\alpha = 0.22$, the value of α_0 implied by typical compatibility relations is approximately 0.40; if one assumes $\alpha_0 = 0.22$ then α is required to be 0.15. The differences indicated by these results are far outside experimental uncertainties in the values of α and α_0 , which are about 0.02 in both cases. Using the relation of Ref. 19, the two limits are even more divergent, and we conclude that the XPS and SXA results are incompatible for Na. This conclusion calls into question the use of a compatibility relation in interpreting edge structure.³⁰

We must therefore look to other sources for the differences between SXE, SXA, and XPS in Na. One possibility is that these differences represent a fundamental failure of the MND model due, for example, to ignoring electron-electron interactions in the conduction band. The fact, however, that all three spectroscopies are well described by a power law suggests that this is not the case. There is a physical difference between these experiments which has not been investigated: namely, the short-time behavior of the local potential. In the MND model the infinite-time response function is needed to evaluate the spectra asymptotically near threshold. In the usual application of the model the infinite-time potential is used to evaluate this response function. Doing so may leave out some of the physics, however, since the response function at a given time can be affected by the behavior of the potential at earlier times.

Both XPS and absorption involve the promotion of a core electron to an unoccupied state. The important difference between the two lies in the energy of that state, i.e., in the velocity of the active electron. In threshold absorption the relevant speed is near the Fermi velocity, while it is many times that in XPS. In threshold absorption the initial net potential created by the transition is dipolar and weak, as opposed to the monopolar XPS potential. In emission the *screened* potential decays away after

the core hole is annihilated. Thus the transient potential is strongest for XPS, intermediate for SXA, and weakest for SXE, correlating directly with the apparent potential strength needed to describe the three experiments.

An early discussion of the bearing of the time dependence of the potential on electron-hole pair (EPH) creation in core spectral measurements was given by Muller-Hartmann, Ramakrishnan, and Toulouse³¹ (MHRT). Their work was later reinterpreted by Gadzuk and Sunjic (GS) in terms of α , the singularity index, the value of which provides a measure of the extent of EHP creation.³² Plasmon creation caused by a core transition has also been extensively investigated theoretically.^{33,34} It has long been known³⁵ that the SXE plasmon satellite (PS) intensity is much weaker than the XPS PS intensity due to the slower active electron.

The GS result was based on a relatively simple form for the time-dependent potential, which is turned on at $t=0$, $V(t) = V_0(1 - e^{-\eta t})$ following the work of MHRT, where $\eta \propto v$, the velocity of the photoelectron. They showed that α varies with photoelectron kinetic energy. This by itself implies that there should be a difference between absorption and high-energy XPS. A potential that can describe the XPS and SXE plasmon satellites, which has a similar form, is

$$V(t) = V_0(1 - e^{-\eta_1 t}) + V_1 e^{-\eta_1 t} - V_2 e^{-\eta_2 t},$$

where η_1 characterizes the time development of the screening of the core hole by the electron sea and η_2 the velocity of the active electron in XPS or absorption. V_1 serves to approximate the unscreened potential of the core hole and V_2 the unscreened potential due to the active electron. V_0 is the screened potential felt at long times.

In order to connect this potential with experiment, we constrain it using the dependence of the XPS PS intensity on photoelectron velocity.³⁴ This leads to the values $V_1 \approx V_2 = 7.5$, $V_0 \approx 0.5$, $\eta_1 \approx \omega_p/2\pi$, and $\eta_2 = 0.37v/\lambda$, where λ is the Thomas-Fermi screening length. These values yield a PS intensity of about 50% of the Na main line at high velocity, and 4% for $v = v_F$, reproducing the results of Ref. 33.

GS have established that the terms containing V_0 are sufficient to show significant effects on EHP creation due to changes in photoelectron velocity in XPS, and their result has received experimental support.³⁶ Since the additional terms involving V_1 and V_2 are so much larger, and vary with the electron velocity much as GS assumed, we suggest that these terms, which are necessary to explain the plasmon satellites, are also responsible for the incompatibility of the threshold exponents between XPS, absorption, and emission. Further theoretical work studying the time-dependent aspects of this problem will be necessary to quantitatively verify this assertion.

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- *Present address: Physics Department, University of Pennsylvania, 209 South 33rd Street, Philadelphia, PA 19104.
- †Present address: Physics Department, FM-15, University of Washington, Seattle, WA 98195.
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