PHYSICAL REVIEW B VOLUME 48, NUMBER 21 1 DECEMBER 1993-I

Analysis of Auger spectra from a He^+ ion near a metal surface

T. Fondén[*] and A. Zwartkruis[†]
Department of Applied Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

(Received 18 June 1993)

Auger rates are computed and analyzed for a He^+ ion in a wide range of ion–metal-surface separations. For neutralization-relevant distances close to the surface, the rate scales approximately quadratically with the density from the electron tails. ($W \propto n^{1.80}$ for $r_s = 2.07\, a_0$ and $W \propto n^{1.93}$ for $r_s = 3.99\, a_0$.) Further away from the surface there is a gradual transition to a more linear scaling of the rate with the electron density ($W \propto n^{1.16}$). Computed Auger spectra are analyzed as well. For all ion-surface distances there is excellent agreement between the spectra and a convolution of the two hole energy distributions, left behind by the metal electrons neutralizing the ion and exciting to the Auger level, respectively. Closer to the surface the two hole spectra are almost identical. This is argued to indicate the localness of the Auger transition around the ion. For larger distances the hole spectra start to differ, indicating that the neutralization becomes increasingly nonlocal. The changeover in the scaling of the rate for larger ion-surface separations is consistent with the spectra analysis. The self-convolutions of the local density of states at the position of the ion do not agree quantitatively with the spectra. Therefore, despite the local character of the Auger process, the variations of the metal orbitals over the region of the ion cannot be neglected.

I. INTRODUCTION

The lifetime of excited and ionized states of atoms and molecules near a solid surface is a controlling factor in many physical phenomena. The physical processes involved in the neutralization of ions impinging with low kinetic energy on a solid surface have extensively been discussed in early works by Hagstrum.[1–4] The important neutralization channels (Fig. 1) are Auger neutralization, and, if energetically allowed, resonant and quasiresonant tunneling. For the total Auger neutralization rate W as a function of the distance Z_{ion} of the ion from the surface, one often assumes a simple exponential dependence

$$W(Z_{\text{ion}}) = A \exp(-a\, Z_{\text{ion}})\,. \qquad (1)$$

Here A and a are free parameters that, e.g., can be fitted to experimental data. In his analysis of the Auger neutralization rate, Hagstrum[1,2,4] assumes that the decrease of the Auger matrix element with increasing ion-surface separation is governed by the decay of the orbital $\mathbf{k}_1$ [see Fig. 2(a)], representing the metal electron that is about to fill the empty atomic level. The rate contains the square of the matrix elements, and, according to Hagstrum, it thus decays away from the surface as the square of the electronic orbitals. As the latter is also true for the density, we then expect that the Auger neutralization rate W scales linearly with the electron density in the vacuum region.

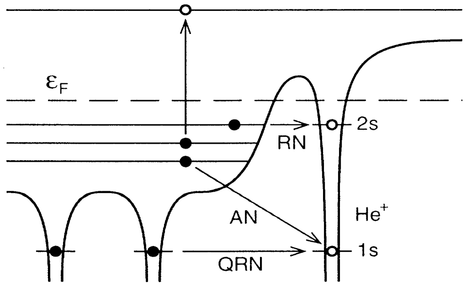

FIG. 1. Different neutralization channels for a He ion outside a surface. Auger neutralization is indicated by AN. RN and QRN denote resonant tunneling and quasiresonant tunneling, respectively.

Unlike Hagstrum, Walkup *et al.*[5] assume the decay away from the surface of both two occupied metal orbitals $\mathbf{k}_1$ and $\mathbf{k}_2$ (see Fig. 2) involved in the Auger process, to be of similar importance for the decrease of the Auger matrix element into the vacuum. In the vacuum region they then expect the Auger neutralization rate to scale as the electron density squared ($W \propto n^2$). Walkup *et al.* obtain experimental support for their assumptions by performing an analysis of the kinetic energy distribution of argon atoms, desorbing from a tungsten surface after ionization and subsequent reneutralization. They parametrize the Auger neutralization rate as in Eq. (1), and obtain a good fit to the experimental kinetic energy distribution of Ar for an Auger decay constant $a = 6$ Å^{-1}. This value corresponds to an Auger rate that decreases with distance from the surface as the electron density to the power 2.4.

Hagstrum[3] developed the technique of measuring the energy distribution of ejected Auger electrons into the so-called ion neutralization spectroscopy (INS). From this spectroscopy one deduces information concerning the surface electronic structure. One writes the measured Auger electron energy spectrum F (corrected for surface escape probabilities, etc.) as a convolution of two functions U_1 and U_2,

0163-1829/93/48(21)/15603(10)/$06.00 48 15 603

$$F(\epsilon_A) = \int_{\max(0,\epsilon_A+\epsilon_g-\epsilon_F)}^{\min(\epsilon_F,\epsilon_A+\epsilon_g)} U_1(\epsilon_1)U_2(\epsilon_A+\epsilon_g-\epsilon_1)d\epsilon_1 \,. \tag{2}$$

The domains of the two functions U_1 and U_2 consist of the occupied portion of the band, i.e., between the bottom of the band ($\epsilon = 0$) and the Fermi level ($\epsilon = \epsilon_F$). The functions U are denoted "transition densities." In their domain they are supposed to describe the density of states, appropriately modified by matrix element effects. If exchange effects are neglected, one of them (say U_1) is taken to be connected with metal electron $\mathbf{k}_1$ to be transferred to the ion. Since the atomic level is strongly localized around the position of the ion, U_1 could be assumed to measure, approximately, the local density of states at the position of the ion. Transition density U_2 is supposed to be related with the metal electron to be excited to the Auger level. The identification[3] of each of U_1 and U_2 with only one of the metal electrons $\mathbf{k}_1$ or $\mathbf{k}_2$, formerly implied an approximation in the form of neglect of exchange effects. However, the recent development of spin-resolved experimental techniques,[6] makes it now in principle possible to concentrate on a channel in which the two metal electrons have opposite spin directions. For that channel one could then disregard exchange without making an approximation.

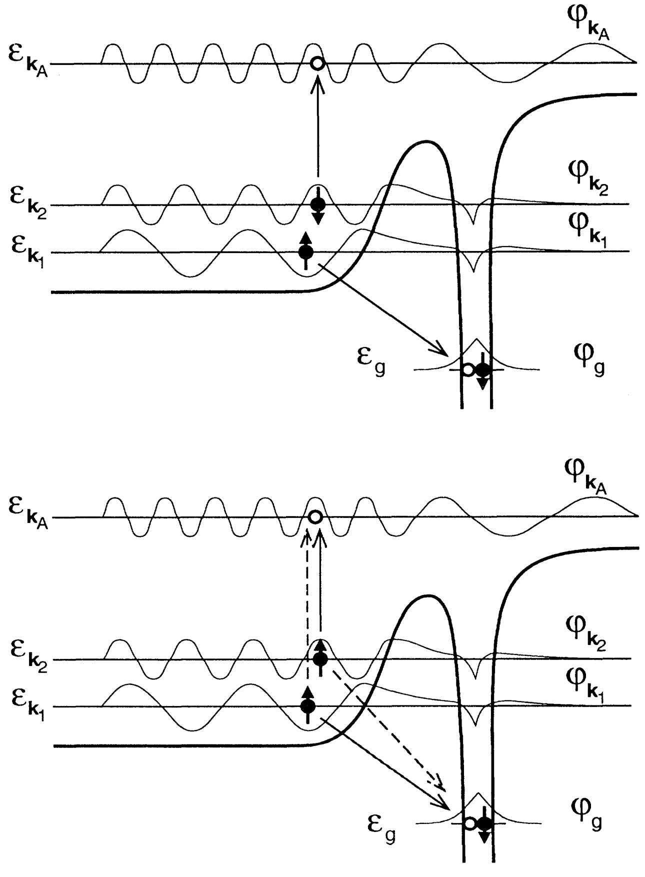

FIG. 2. Potential energy diagram showing Auger neutralization of a spin-down polarized He ion outside a metal surface. In (a) a spin-down Auger electron is generated. The two involved electrons possess different spin directions and are distinguishable. In (b) a spin-up electron is produced. The spin directions of the two involved electrons are now the same. Therefore both the direct process (solid arrows) and the exchange process (dashed arrows) have to be considered.

Some indirect experimental support for Hagstrum's assumption leading to linear scaling with electron density, is provided by Appelbaum and Hamann's[7] comparison of measured kinetic energy distributions of ejected Auger electrons to calculated local densities of states for clean and hydrogen covered silicon surfaces. In their analysis of spectra Appelbaum and Hamann[7] arrive at an expression essentially of the same form as Eq. (2), where now U_1 represents the local density of states at the position of the ion and U_2 the local density of states at some *a priori* unknown position $\mathbf{R}^*$. By comparing experimental Auger spectra to convolutions of calculated local densities of states for different positions $\mathbf{R}^*$, they find the best agreement by taking U_2 as the local density of states at a position $\mathbf{R}^*$ that is significantly closer to the surface than the ion. A possible interpretation of this result is that the decay of the orbital of the metal state $\mathbf{k}_2$, to be excited to the Auger level, is not probed at the position of the ion. As such, the result could be considered as a support for Hagstrum's scaling $W \propto n$. Below we will further comment on the procedure of Appelbaum and Hamann.

In Refs. 8 and 9 we have presented a model and some computed results for Auger neutralization. Even when improving upon previously published models (see, e.g., Refs. 10–12) our model is still approximate and has a qualitative rather than quantitative accuracy. One of the main approximations in our method consists of the use of metal orbitals from an unperturbed jellium surface. In reality the metal surface is perturbed by the attractive electrical potential from the positive He ion. Then the electron density at the position of the ion is larger than assumed here, and the real rate is larger than the computed one. Yet, as regards the qualitative aspects of the total rate as a function of the ion-surface distance, we have earlier[9] shown our model to be robust. Namely, we have simulated some of the effects from the ion on the metal orbitals by perturbing the latter by a charge sheet. Then the total rate was significantly increased, but its qualitative behavior as a function of the ion-surface separation remained essentially unchanged. The spectra on the other hand were seen to be more sensitive to the perturbation by the electric field.

In this article we shall not as much compare computed spectra with experiment as with theoretically computed quantities within the same model. We will focus on a discussion and interpretation of the Auger process within the one-electron approximation for an unperturbed surface. In particular we will consider the connection between the spectra and the localness of the Auger neutralization process, i.e., to what extent the Auger matrix elements probe the metal orbitals in only a limited region around the ion. Spectra from the unperturbed jellium are used in this article. Further approximations in our model consist, e.g., of the use of the one-electron picture. Hereby certain subtle many-particle effects,[13] present in a more exact treatment of the attractive ion potential in the Auger calculation, are excluded. Inelastic scattering of Auger electrons, as recently shown to be important by Salmi,[14] is left out as well. Section II presents results for computed total rates and spectra. Section III gives a discussion and interpretation of these. Our conclusions are summarized in Sec. IV.

II. CALCULATION AND RESULTS

Our model and some results for Auger neutralization rates in the case of a helium ion near a simple metal surface have been presented in Refs. 8 and 9. The Auger rate is evaluated from the Golden Rule formula in a one-electron-like model. The electron-electron interaction is taken as an unscreened Coulomb potential. The localized orbital of the ion is described by a 1s Slater orbital. The metal orbitals are taken from the jellium model[15] for an unperturbed simple metal surface. However, a correction is applied to the orbital describing the metal electron to be transferred to the ion by orthogonalizing it to the localized orbital. Using these approximate orbitals, the matrix elements are evaluated and the integrations over all allowed final states are performed without any further approximations. Further details on the theoretical model can be found in Ref. 8.

A. Results for the total Auger rate

In our previous papers[8,9] the total Auger rates for metals of different bulk electronic densities are rather well described by the simple exponential parametrization of Eq. (1). In the vacuum region the values of the decay constant a correspond to a rate that scales approximately as the electron density squared. In Fig. 3, for a larger region of space than was presented in Refs. 8 and 9, we show computed total Auger rates for a He$^+$ ion outside jellium substrates with electron densities corresponding to those of Al and Na ($r_s = 2.07a_0$ and $3.99a_0$, respectively). As presented before, in an intermediate region not too far away from the surface the rate decays exponentially with distance. For larger distances the total rate as a function of distance deviates from the original exponential behavior, and decreases less rapidly. For the largest distances in Fig. 3 the rate seems to enter an asymptotic region where it again decreases exponentially with distance. The rate of decrease is now slower than it is close to the surface. For the regions of Fig. 3 where the rate is exponentially declining, Fig. 4 shows that there is a scaling between the density from the electron tails in the vacuum and the Auger rate. For smaller and larger distances, the exact scaling relations are denoted in this figure. Close to the surface the rate scales quadratically with the density and further away the scaling is close to linear ($W \propto n^{1.16}$). As in Fig. 4 the curves for Al and Na differ, we see that, even if there is scaling, there is no universal relation between density and rate.

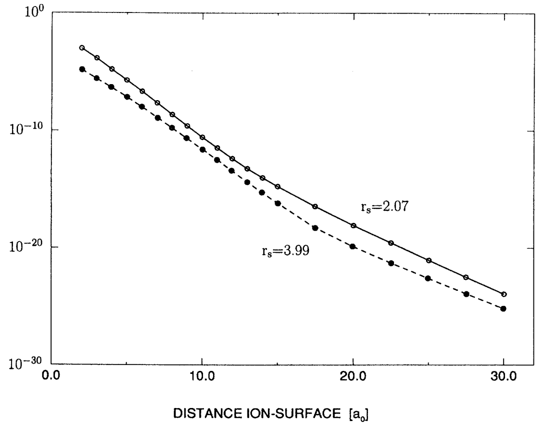

FIG. 3. The total Auger rate as a function of the distance Z_{ion} from the ion to the jellium edge. Results are shown for semi-infinite jellia with bulk densities of $r_s = 2.07a_0$ and $3.99a_0$, corresponding to the bulk densities of Al and Na, respectively. Each curve contains two different parts of approximately exponential decay. The decay constants for these parts are different.

B. Results for Auger spectra

In addition to the total rate we have also calculated the energy distributions (spectra), F, of the Auger electrons produced and emitted in the neutralization process. The Golden Rule expressions for the resulting *produced* Auger currents per unit energy for spin-up and spin-down electrons (with spin-direction convention as in Fig. 2) are in Rydberg units:

$$F_\uparrow(\epsilon_A) = \pi \int d^3k_1 d^3k_2 d^3k_A \; \delta(E_I - E_F) \times \delta(\epsilon_{\mathbf{k}_A} - \epsilon_A) \mid v_{\mathbf{k}_A,g,\mathbf{k}_1,\mathbf{k}_2} - v_{\mathbf{k}_A,g,\mathbf{k}_2,\mathbf{k}_1} \mid^2 \tag{3}$$

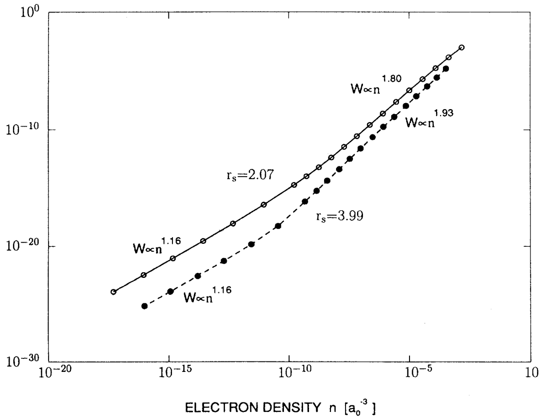

FIG. 4. Total Auger rates from Fig. 3, now depicted as a function of the density n of the electron tails in the vacuum region. For the regions that show exponential decay in Fig. 3, the scaling of the rate with the density is indicated. There is a gradual transition in the rate between these regions.

and

$$F_{\downarrow}(\epsilon_A) = \pi \int d^3k_1 d^3k_2 d^3k_A \, \delta(E_I - E_F) \times \delta(\epsilon_{\mathbf{k}_A} - \epsilon_A) \, 2 \mid v_{\mathbf{k}_A,g,\mathbf{k}_1,\mathbf{k}_2} \mid^2 . \tag{4}$$

Here (see Ref. 8) v is the electron-electron interaction matrix element (Auger matrix element) and E_I and E_F are the total energies of the initial and final states, respectively. The integrations over $\mathbf{k}_1$ and $\mathbf{k}_2$ are restricted to within the Fermi sphere. The integration over the Auger electron wave vector $\mathbf{k}_A$ includes all wave vectors outside the Fermi sphere. The corresponding expressions for the *emitted* Auger electrons are obtained by restricting the integration over $\mathbf{k}_A$ to electrons that surmount the surface barrier, i.e., to electrons with $k_{Az} > \sqrt{V_{\text{vac}}}$. Here k_{Az} is the component of the Auger electron wave vector perpendicular to the surface and V_{vac} the value of the vacuum level relative to the bottom of the band. For bulk r_s values of 2.07 and $3.99a_0$, we show in Fig. 5 Auger spectra for a He^+ ion at a distance of 5.0, 8.0, and $20.0a_0$ outside the jellium surface. Each subfigure of Fig. 5 contains the spectra for produced spin-up and spin-down Auger electrons, and also spectra for emitted spin-up and spin-down electrons. For the two shortest ion-surface separations the intensity of the spin-down Auger electrons is much larger than of the spin-up Auger electrons, in agreement with earlier results.[14]

Now both in Figs. 6 and 7 and in the following discussion we limit ourselves to the spin-down spectra. For a spin-down polarized He beam and in the spin-direction convention from Fig. 2 this means that the two involved electrons have different spin direction and thus can be treated as distinguishable. Figure 6 includes the spectra of produced (spin-down) electrons and the self-convolution of the local density of states (LDOS) at the position of the ion. It is seen that the Auger spectra deviate from the self-convoluted LDOS. For the neutralization relevant distances of 5.0 and $8.0a_0$, the differences are especially large for the $r_s = 2.07a_0$ case. This means that it is not possible to take the transition densities U_1 and U_2 (at least not both of them) to be equal to the LDOS at the position of the ion.

In addition to the spectra of Auger electrons we have calculated the spectra of holes produced in the metal

$$J_{\downarrow,h_1}(\epsilon) = \pi \int d^3k_1 d^3k_2 d^3k_A \, \delta(E_I - E_F) \times \delta(\epsilon_{\mathbf{k}_1} - \epsilon) \, 2 \mid v_{\mathbf{k}_A,g,\mathbf{k}_1,\mathbf{k}_2} \mid^2 , \tag{5}$$

$$J_{\downarrow,h_2}(\epsilon) = \pi \int d^3k_1 d^3k_2 d^3k_A \, \delta(E_I - E_F) \times \delta(\epsilon_{\mathbf{k}_2} - \epsilon) \, 2 \mid v_{\mathbf{k}_A,g,\mathbf{k}_1,\mathbf{k}_2} \mid^2 . \tag{6}$$

Here $J_{\downarrow,h_1}$ is the energy distribution (spectrum) of holes

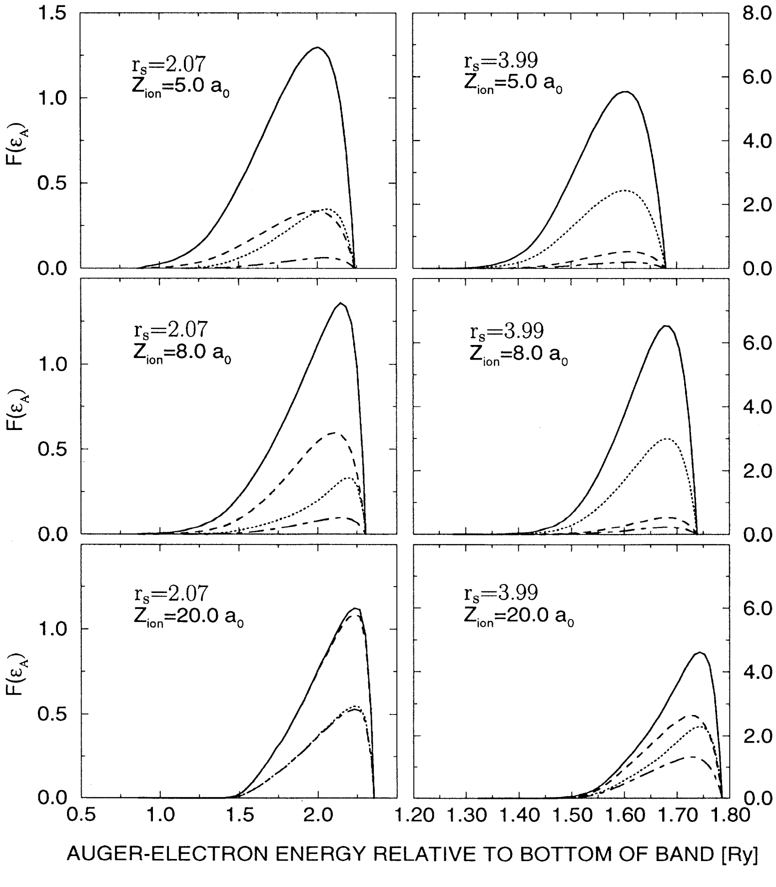

FIG. 5. Energy distributions (spectra) of produced spin-down Auger electrons (solid lines), produced spin-up Auger electrons (dashed lines), emitted spin-down Auger electrons (dotted lines), and emitted spin-up Auger electrons (dash-dotted lines), respectively. The spectra are shown for Al and Na, for several distances Z_{ion} from the ion to the jellium edge. For each of these distances, the normalization has been chosen such that the sum of the areas under the produced spin-down and produced spin-up curves equals unity.

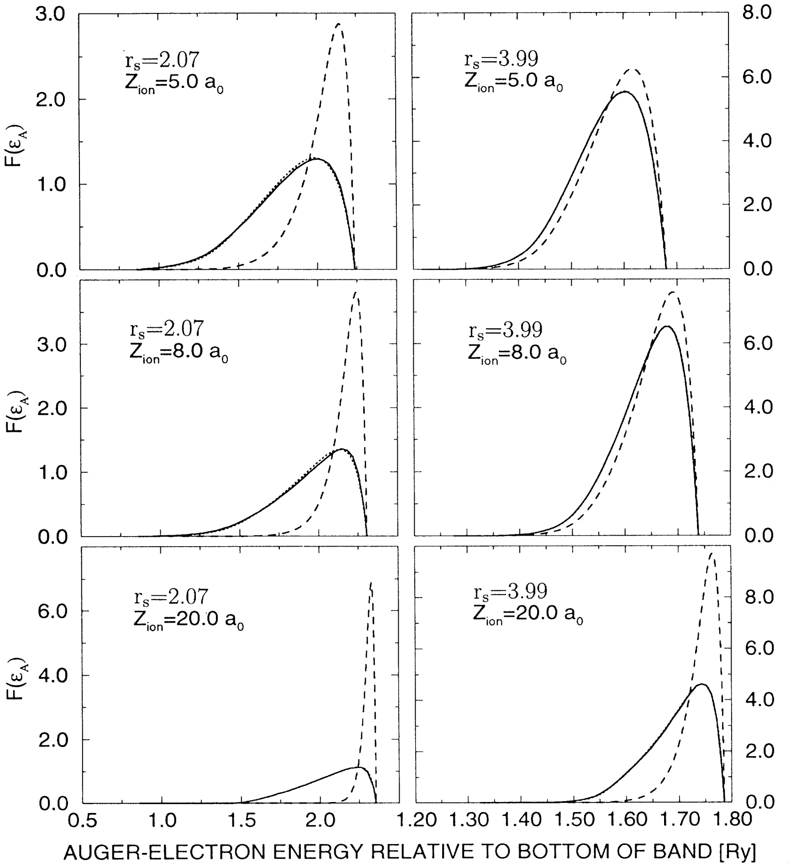

FIG. 6. Comparison between the spectrum of produced spin-down Auger electrons (solid line) from Fig. 5 and the convolution (dotted line) of the spin-down "hole" spectra $J_{\downarrow,h_1}(\epsilon)$ and $J_{\downarrow,h_2}(\epsilon)$. For most distances the graphs overlap. For each distance, the self-convolution of the local density of states (dashed line) is also plotted. The convolutions in each figure are normalized to have the same area as the corresponding spectrum of produced spin-down Auger electrons.

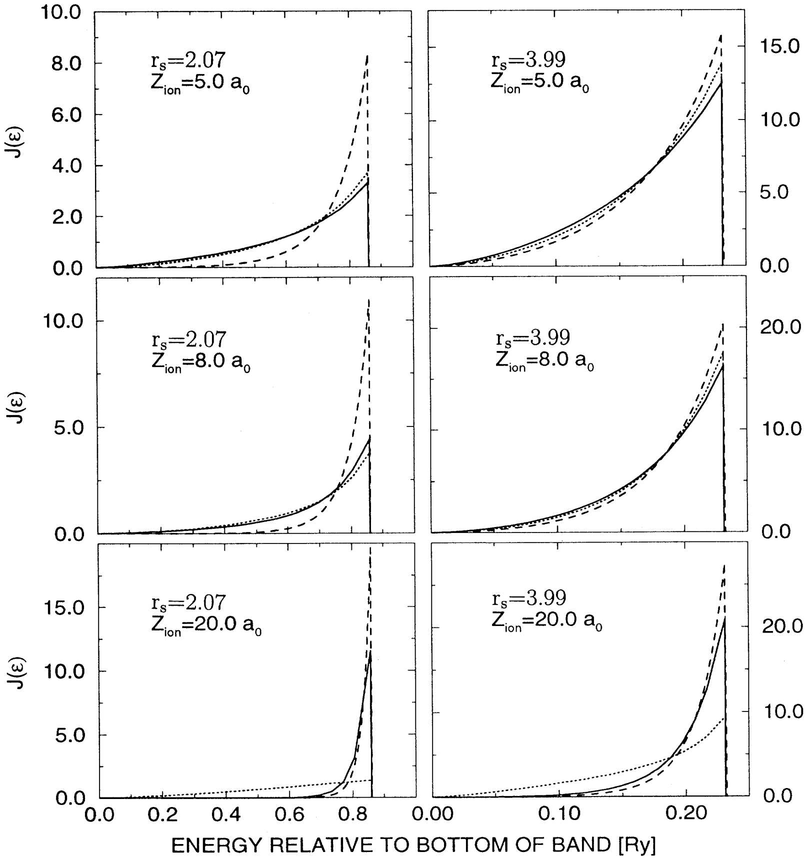

FIG. 7. Spectra of holes that are left in the metal after the production of spin-down Auger electrons. The spectrum $J_{\downarrow,h_1}(\epsilon)$ (solid line) comes from the electrons neutralizing the ion, the spectrum $J_{\downarrow,h_2}(\epsilon)$ (dotted line) is left behind by the electrons that are excited as Auger electrons. These spectra can be compared with the local density of states (dashed line) for the metal at the position of the ion. The local density of states is normalized to have the same area as the two hole spectra.

left behind by the electrons that were transferred to the helium ion. $J_{\downarrow,h_2}$ gives the energy distribution of holes left behind by electrons that were excited to the Auger level. In Fig. 7 we show these spectra of holes for two r_s and three ion-surface separations. The two different kinds of hole spectra are seen to be almost identical when the ion is situated not too far away from the surface, i.e., the region where the total Auger rate scales approximately quadratically with the electron density. For larger ion-surface separations, however, the two kinds of hole spectra look very different. The one corresponding to the electrons neutralizing the ion is much more peaked towards the Fermi level than the one corresponding to the electrons being excited to the Auger level. Local densities of states (normalized to have the same area as the hole spectra) are also plotted in Fig. 7. They are more peaked towards the Fermi energy than the corresponding transition densities. As in Fig. 6, the differences in Fig. 7 are the largest for the $r_s = 2.07a_0$ case. Upon inclusion in Fig. 6 of the convolution [see Eq. (2)] of the two hole spectra given by Eqs. (5) and (6), it turns out that *for all distances* the Auger spectrum is well represented by this convolution. That is, the transition densities U_1 and U_2 turn out to be well approximated by the corresponding hole spectra.

III. DISCUSSION OF RESULTS

In Fig. 3 there is a region of space where the total rate scales approximately linearly with the electron density, and thus behaves according to Hagstrum's assumption that only the decay of the orbital $\varphi_{\mathbf{k}_1}$ into the vacuum is noticeable in the rate. From the value of the high-energy cutoff in experimental Auger spectra, Hagstrum[1,4] however estimates that the neutralization of an ion typically takes place for an ion-surface separation (as measured from the image plane) of around $4a_0$ (i.e., roughly 5–$6a_0$ outside the jellium edge). In that region our results show an approximately quadratic scaling of the total Auger rate with the electron density, which indicates that both the decay of $\varphi_{\mathbf{k}_1}$ and of $\varphi_{\mathbf{k}_2}$ away from the surface are important in determining the decrease in the rate for increasing ion-surface separation.

In order to discuss the rates and spectra, we consider the Auger matrix element

$$v_{\mathbf{k}_A,g,\mathbf{k}_1,\mathbf{k}_2} = \int\int d^3r d^3r' \; \varphi^*_{\mathbf{k}_A}(\mathbf{r})\varphi^*_g(\mathbf{r}')\frac{2}{|\mathbf{r}-\mathbf{r}'|}\varphi_{\mathbf{k}_1}(\mathbf{r}')\varphi_{\mathbf{k}_2}(\mathbf{r}) = \int d^3r \; \varphi^*_{\mathbf{k}_A}(\mathbf{r})v_{g,\mathbf{k}_1}(\mathbf{r})\varphi_{\mathbf{k}_2}(\mathbf{r})\,, \tag{7}$$

where $v_{g,\mathbf{k}_1}$ is the resulting potential from the charge density fluctuation representing the transfer of an electron from the metal orbital $\varphi_{\mathbf{k}_1}$ to the atomic orbital φ_g,

$$v_{g,\mathbf{k}_1}(\mathbf{r}) = \int d^3r' \; \frac{2}{|\mathbf{r}-\mathbf{r}'|}\varphi^*_g(\mathbf{r}')\varphi_{\mathbf{k}_1}(\mathbf{r}')\,. \tag{8}$$

A. Total rates

Since the "charge distribution" $\varphi^*_g(\mathbf{r})\varphi_{\mathbf{k}_1}(\mathbf{r})$ is strongly localized around the position of the ion, the potential $v_{g,\mathbf{k}_1}(\mathbf{r})$ should obtain its maximum value there. This value, and hence the matrix element $v_{\mathbf{k}_A,g,\mathbf{k}_1,\mathbf{k}_2}$, are then approximately proportional to the value of $\varphi_{\mathbf{k}_1}$ at the position of the ion.

If, averaged over all allowed values of $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_A$, the peaking of $v_{g,\mathbf{k}_1}$ is the dominant factor in determining where the integrand $\varphi^*_{\mathbf{k}_A}(\mathbf{r})v_{g,\mathbf{k}_1}(\mathbf{r})\varphi_{\mathbf{k}_2}(\mathbf{r})$ gives its main contribution to the integral (7), then one should expect the matrix element to also be approximately proportional to the value of the wave function $\varphi_{\mathbf{k}_2}(\mathbf{r})$ at the position of the ion. In that case the Auger neutralization rate scales as the square of the electron density. This is what indeed is seen in our calculated rates for ion-surface distances less than approximately $10a_0$.

On the other hand we know that the asymptotic rate of decrease of the potential $v_{g,\mathbf{k}_1}(\mathbf{r})$ away from the position of the ion is rather slow. The monopole moment of the "charge distribution" $\varphi^*_g(\mathbf{r})\varphi_{\mathbf{k}_1}(\mathbf{r})$ is zero due to wavefunction orthogonality.[8] Yet, the dipole moment does not vanish, and $v_{g,\mathbf{k}_1}(\mathbf{r})$ therefore decreases asymptotically as $|\mathbf{r}-\mathbf{R}_{\text{ion}}|^{-2}$. The growth of the orbital $\varphi_{\mathbf{k}_2}$ towards the surface is exponential. Thus, *for large enough ion-surface separations*, this exponential growth of $\varphi_{\mathbf{k}_2}(\mathbf{r})$ always wins over the mere algebraic decrease of $v_{g,\mathbf{k}_1}(\mathbf{r})$ towards the surface. Then the product $v_{g,\mathbf{k}_1}(\mathbf{r})\varphi_{\mathbf{k}_2}(\mathbf{r})$ does not have its maximum around the position of the ion, but has it instead in the neighborhood of the surface where the exponential growth of $\varphi_{\mathbf{k}_2}(\mathbf{r})$ ends. For large enough ion-surface separations one therefore expects the functional dependence of the matrix element on Z_{ion} to be dominated by the orbital $\varphi_{\mathbf{k}_1}$ only. Then the Auger neutralization rate scales linearly with the electron density. It is this effect that is seen in our calculated rates for the largest ion-surface distances.

B. Spectra

Our interpretation from the total rate result that in the intermediate distance regime the Auger matrix element is dependent on the values of both two originally occupied metal orbitals at the position of the ion, but for the very largest distances only on the value of the neutralizing orbital is further supported by the calculated spectra.

As is seen in Fig. 6, the (spin-down) Auger spectra can be deconvoluted according to formula (2) by taking the transition densities U_1 and U_2 as the energy spectra of the holes left behind by the electrons transferred to the ion and the Auger level, respectively. In the distance regime where the rate scales quadratically with the electron density, the two transition densities U_1 and U_2 look almost identical (see Fig. 7). Both of them peak towards higher energies. This can be understood from the fact that (for given direction of the wave vector) metal orbitals of higher energy decay less rapidly away from the surface. The similarity between the two transition densities U_1 and U_2 indicates that the decay of both two metal electron orbitals in the vacuum region is of approximately equal importance for the matrix element. Hence, in the intermediate distance regime, the values of the two metal orbitals at (approximately) the position of the ion are the important ones, i.e., the peaking of $v_{g,\mathbf{k}_1}$ in the vicinity of the ion is sufficiently strong to win over the increase of the wave functions $\varphi_{\mathbf{k}_2}$ away from the ion towards the surface.

For very large ion-surface separations (see the graphs for $Z_{\text{ion}} = 20.0a_0$ in Fig. 7), the transition density U_2, related to $\varphi_{\mathbf{k}_2}$, peaks significantly less towards higher energies than does the transition density U_1 (connected with $\varphi_{\mathbf{k}_1}$). A natural interpretation of this fact is that the matrix element is less sensitive to the decay of the metal orbital $\varphi_{\mathbf{k}_2}$ as measured at the position of the ion. That is, the exponential growth of $\varphi_{\mathbf{k}_2}$ now stretches over such long distance from the ion to the surface that it wins over the merely algebraic decrease of $v_{g,\mathbf{k}_1}$. Consequently, the main contributions to the matrix element integral (7) do not come from the vicinity of the ion, but from a region close to the surface.

It should be noted though, that the turnover from a locally occurring Auger process to a nonlocal one is gradual. The Auger rates and spectra are obtained by integrating over the final states (i.e., over allowed values of $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_A$). Whether an individual matrix element probes the metal orbital $\varphi_{\mathbf{k}_2}(\mathbf{r})$ mostly at positions close to the ion or at positions close to the surface, depends not only on the ion-surface separation but also on the values of the involved wave vectors. In the integration over final states, the overall localness of the Auger process is determined from the fact whether integral Eq. (7) gets its dominating contributions from matrix elements which probe positions close to the ion or close to the surface. In the spectra from Fig. 7 for $Z_{\text{ion}} = 20.0a_0$ the transition density $J_{\downarrow,h_2}$ is much less peaked towards the Fermi energy than $J_{\downarrow,h_1}$. The total rate does not yet scale linearly with the electron density though. Thus the Auger process is here still in the turnover region where, in the integration over final states, there are important contributions both from matrix elements that probe the orbital $\varphi_{\mathbf{k}_2}$ mostly in the vicinity of the ion and of those that probe $\varphi_{\mathbf{k}_2}$ in the vicinity of the surface.

For the intermediate ion-surface distances where the above reasoning stresses the importance of the values of both involved metal orbitals *at the position of the ion*, Appelbaum and Hamann[7] arrive at a conclusion different from ours. For the neutralizing electron they take the transition density U_1 to be approximated by the calculated LDOS at the position of the ion. The transition density U_2, connected with the metal electron that is excited to the Auger level, is approximated by the calculated LDOS at some *a priori* unknown position $\mathbf{R}^*$. Determining $\mathbf{R}^*$ from fitting the experimental spectra to a convolution of calculated LDOS, gives a value for $\mathbf{R}^*$ that lies significantly closer towards the surface than the ion. Appelbaum and Hamann's result then means that *even for intermediate ion-surface distances* the Auger matrix element would only be sensitive to the value of the neutralizing electron orbital $\varphi_{\mathbf{k}_1}$ at the position of the ion. The value of the metal orbital $\varphi_{\mathbf{k}_2}$ at the same position would not directly enter the matrix element.

Appelbaum and Hamann have investigated spectra for a silicon surface rather than for a jellium surface. Yet we think that a comparison between their work and ours is relevant as the qualitative behavior of the vacuum tails of the wave functions for both cases should be sufficiently similar. Our interpretation differs then from their one by the fact that we do not directly identify the transition densities U with local densities of states. Rather we have identified them (in a numerical way) with the hole spectra. For intermediate ion-surface separations the hole spectra U_1 and U_2 are virtually identical. However, even though the hole spectra do show the qualitative behavior of LDOS in peaking towards higher energies, they do not always form a good approximation to the LDOS in a quantitative sense. The LDOS is seen to be the most strongly peaked of them. Thus the different identification of the transition densities leads to different interpretations of the localness for the Auger neutralization process.

If the Auger spectrum is available over the whole energy interval $[-\epsilon_g, 2\epsilon_F - \epsilon_g]$, it can in principle be deconvoluted, and for the energy interval $[0, \epsilon_F]$ two transition densities U_1 and U_2 can be determined. In practice, however, only the Auger spectrum for energies larger than the vacuum level can be measured. Then there is insufficient experimental information available for a determination of the transition densities. The approach taken by Hagstrum[3] is then to make the approximation of considering the two transition densities as equal and to use only the part of the Auger spectrum in the energy interval $[\epsilon_F - \epsilon_g, 2\epsilon_F - \epsilon_g]$. He justifies this approximation partly by means of numerical examples. If a function F, created as convolution of two somewhat different functions U_1 and U_2, is deconvoluted in terms of a single function U, then this function is found to be not too different from the geometrical mean of U_1 and U_2. The fact that for neutralization-relevant ion-surface separations the two hole spectra U_1 and U_2 in our calculation turn out to be almost identical, provides some additional support for this approach of Hagstrum.

In the neutralization-relevant ion-surface distance regime the two transition densities U_1 and U_2 are almost identical, but they are not equal to the LDOS (the difference is largest for high density substrates). We now show that this fact implies that the metal orbitals cannot be approximated by a constant over the extent of the atomic orbital.

The orbital $\varphi_{\mathbf{k}_1}$ is constructed from the unperturbed jellium orbital $\varphi^0_{\mathbf{k}_1}$ by orthogonalizing[8] it against the atomic orbital φ_g. Since φ_g is spherically symmetric, the "charge density" $\varphi^*_g\varphi_{\mathbf{k}_1}$ would also become spherically symmetric if $\varphi^0_{\mathbf{k}_1}$ were constant over the extent of the atomic orbital. In that case all multipole moments of the "charge distribution" $\varphi_g^* \varphi_{\mathbf{k}_1}$ would vanish. The monopole moment would be zero due to wave-function orthogonality,[8] and all higher-order multipole moments would vanish because of the spherical symmetry of the charge density. The potential $v_{g,\mathbf{k}_1}$ would become as localized as the atomic orbital φ_g, i.e., different from zero only within the extent of the atomic orbital φ_g. This conclusion holds if $\varphi^0_{\mathbf{k}_1}$ can be considered as constant over the extent of the atomic orbital. Because in that case both originally occupied metal orbitals in matrix element (7) are probed over the same spatial region (the range of either φ_g or equivalently of $v_{g,\mathbf{k}_1}$), it is then justified to assume also the $\mathbf{k}_2$ orbital to be constant over that region.

Finally, also the Auger orbital $\varphi_{\mathbf{k}_A}$ in matrix element (7) would only be probed over the same limited region. Due to its higher energy though, $\varphi_{\mathbf{k}_A}$ may have faster spatial variations than either the $\mathbf{k}_1$ or the $\mathbf{k}_2$ orbital. Hence it may be necessary to include terms of higher than zeroth order in a Taylor expansion of $\varphi_{\mathbf{k}_A}$. Note however that the spherical symmetry around the ion of $v_{g,\mathbf{k}_1}$ and $\varphi_{\mathbf{k}_2}$ makes the first-order (gradient) term in the Taylor expansion of $\varphi_{\mathbf{k}_A}$ to have vanishing contribution in matrix element (7).

In conclusion we see that if the orbitals $\varphi^0_{\mathbf{k}_{1,2}}$ vary slowly enough to be described by a zeroth-order Taylor expansion around the position of the ion, and the orbital $\varphi_{\mathbf{k}_A}$ by a first-order Taylor expansion, then the matrix element can be written as (C is a constant)

$$v_{\mathbf{k}_A,g,\mathbf{k}_1,\mathbf{k}_2} = C\, \varphi^*_{\mathbf{k}_A}(\mathbf{R}_{\text{ion}})\, \varphi^0_{\mathbf{k}_2}(\mathbf{R}_{\text{ion}})\, \varphi^0_{\mathbf{k}_1}(\mathbf{R}_{\text{ion}})\,. \quad (9)$$

In such an approximation the Auger spectrum equals the self-convoluted LDOS of the occupied part of the band times the LDOS at the energy of the Auger electron. Since the latter can be taken as approximately constant (for energies somewhat above the vacuum level), the transition densities U_1 and U_2 would then both equal the LDOS at the position of the ion. Our calculated spectra show that (particularly for high-density metals) this is not true and thus indicate that a zeroth-order Taylor expansion of $\varphi^0_{\mathbf{k}_1}$ is not enough. Not only the value of the metal orbitals right at the position of the ion seems to be of importance, but also their change over the extent of the atomic orbital (e.g., their gradient).

A possible hint as to why the transition density U_1 is not as strongly peaked towards higher energies as the LDOS at the position of the ion may be obtained from similar reasoning. Metal orbitals $\varphi^0_{\mathbf{k}_1}$ with low "perpendicular energy" k^2_{1z} have a vacuum tail that decays fastly into the vacuum. Hence, in the direction perpendicular to the surface, the component of the dipole moment of their "normalized charge distributions" $\varphi_g{}^*(\mathbf{r})\varphi_{\mathbf{k}_1}(\mathbf{r})/\varphi_{\mathbf{k}_1}(\mathbf{R}_{\text{ion}})$ is relatively large. In other words, the component of the dipole moment of $\varphi_g^*\varphi_{\mathbf{k}_1}$ pointing towards the surface decreases less rapidly with decreasing perpendicular energy than does $\varphi^0_{\mathbf{k}_1}(\mathbf{R}_{\text{ion}})$.

A finite dipole moment implies that the potential $v_{g,\mathbf{k}_1}(\mathbf{r})$ decreases less rapidly with distance from the ion than the atomic orbital [as $\mid \mathbf{r} - \mathbf{R}_{\text{ion}} \mid^{-2}$ compared to $\exp(-\gamma \mid \mathbf{r} - \mathbf{R}_{\text{ion}} \mid)$]. In addition, the gradient of $\varphi_{\mathbf{k}_1}$ moves the center of gravity of $\mid \varphi_g^*(\mathbf{r})\varphi_{\mathbf{k}_1}(\mathbf{r}) \mid$, and thus also $v_{g,\mathbf{k}_1}(\mathbf{r})$ slightly from the ionic position towards the surface. The peak in $v_{g,\mathbf{k}_1}(\mathbf{r})$ therefore both widens, and also slightly shifts towards the surface, because of the evanescent character of $\varphi_{\mathbf{k}_1}$ and its finite gradient. The integral Eq. (7) can then pick up more contributions from the region between the ion and the surface, where the metal orbital $\varphi_{\mathbf{k}_2}(\mathbf{r})$ has not yet decayed as much as at $\mathbf{r} = \mathbf{R}_{\text{ion}}$. One would then expect a larger value of the matrix element than if it would be completely determined by the value of the orbital at the place of the ion. This explains why the transition density U_1 is not as peaked towards the higher energies as the LDOS at the position of the ion.

Also the transition density U_2 (related to $\varphi_{\mathbf{k}_2}$) is less strongly peaked towards higher energies than the LDOS. We can understand this from the fact that, particularly for those matrix elements where $\varphi_{\mathbf{k}_1}$ has a fast decay away from the surface, $\varphi_{\mathbf{k}_2}(\mathbf{r})$ in the integral Eq. (7) is effectively probed somewhat away from the ion towards the jellium surface. At a position closer to the surface $\varphi_{\mathbf{k}_2}(\mathbf{r})$ varies less rapidly as a function of k^2_{2z} ("perpendicular energy"). This then causes the transition density U_2 to be less peaked towards higher energies than the LDOS at the ionic position.

Within this framework also the difference between the spectra for high and low r_s materials can now be understood. The $r_s = 2.07a_0$ jellium surface has a work function of 0.284 Ry wheras the $r_s = 3.99a_0$ one has a work function of only 0.226 Ry. The larger work function for the $r_s = 2.07a_0$ jellium surface makes its orbitals decay faster away from the surface and hence gives a larger deviation of the Auger spectrum from the self-convolution of the LDOS at the position of the ion.

Even if the dipole component (pointing towards the surface) of the transition potential $v_{g,\mathbf{k}_1}(\mathbf{r})$ is important, we still imagine the Auger process to occur rather locally for the neutralization-important case where the ion-surface separation is not too large. For not too large ion-surface distances, the exponentially growing $\varphi_{\mathbf{k}_2}(\mathbf{r})$ is not yet dominating over the algebraically decaying $v_{g,\mathbf{k}_1}(\mathbf{r})$. The integral Eq. (7) may pick up contributions from positions between the ion and the surface. In the integration over allowed final states though, the dominating contribution comes from matrix elements where the integral Eq. (7) gets its most important contributions from positions that are much closer to the ion than to the surface.

Here we would like to comment on the approximate method for computing Auger neutralization rates, that was recently proposed by Alducin, Arnau, and Echenique[16] and Lorente and Monreal.[17,18] The approximation consists of embedding the ion in a homogeneous electron gas corresponding to the local density at the position of the ion, and deriving the Auger rate from this simpler situation. Implicit in such an approximation is of course the assumption that the Auger process occurs locally. Our above results could then be considered as a partial justification for their approximation in the case of not too large ion-surface separations. However, from our computational experiences it seems hard to derive any systematic corrections to this zeroth-order approach that would take into account the evanescent character of the true metal orbitals.

IV. CONCLUSIONS

We have calculated total Auger neutralization rates as well as Auger electron energy spectra for a He^+ ion outside a simple metal surface. As a function of the distance between the surface and the ion, Z_{ion}, the rate shows a varying character. In an intermediate distance range $(4.0a_0 < Z_{\text{ion}} < 10.0a_0)$, the rate scales approximately quadratically with the electron density. On the other hand, for the largest ion-surface separations studied, $Z_{\text{ion}} \approx 30a_0$, the rate seems to enter an asymptotic region where an approximately linear scaling of the rate with the electron density occurs. The Auger electron energy spectrum was found to equal the convolution of two "transition densities" (here denoted as U_1 and U_2) over the domain of the occupied portion of the band. In the first mentioned distance regime the Auger electron energy spectra may be deconvoluted into two almost identical transition densities. For larger ion-surface distances, on the other hand, the function U_1 (corresponding to the metal electron to be transferred to the ion) is seen to be significantly narrower than the function U_2 (corresponding to the metal electron to be excited to the Auger level). Both the results for the total rate and for the spectra are consistent with an interpretation that the Auger matrix element in the intermediate distance regime is sensitively dependent on the values of both involved metal orbitals, evaluated at positions close to the ion. For larger ion-surface distances, however, the matrix element is sensitively dependent only on the value of the orbital (at the position of the ion), representing the metal electron about to neutralize the ion. For this case the contribution to the matrix element from the orbital representing the metal electron to be excited to the Auger level comes from a region closer to the surface.

Expressing our conclusions in a somewhat more loose sense, we might say that, for not too large ion-surface separations, the Auger electron is excited in the neighborhood of the ion. For larger ion-surface separations the Auger electron is instead excited further away from the ion.

Our model is similar to the one used by Hagstrum[2,3] in his interpretation of ion neutralization Auger spectra. A similar analysis has also been applied to Auger neutralization in the context of metastable atom spectroscopy by Sesselmann *et al.*[19] However, Hagstrum has never evaluated matrix elements explicitly. Instead, he has discussed these in terms of the value of the orbital representing the neutralizing electron [$\mathbf{k}_1$ in Fig. 2(a)] at the position of the ion, and the effective range of interaction between the two involved metal electrons. Our work indicates that in the interesting distance regime *both* involved metal orbitals are probed mainly in the vicinity of the ion. According to Hagstrum's arguments, this would imply that the Auger spectrum would deconvolute into two "transition densities" both approximately equal to the local density of states at the position of the ion. In our analysis we indeed find two almost identical transition densities, but these are not equal to the LDOS. We think that the difference comes from the fact that the metal orbitals cannot be considered constant over the extent of the ionic orbital. Thus for quantitative purposes, Hagstrum's approach of considering only the value of the neutralizing orbital at the position of the ion seems an oversimplification. Also first and higher derivatives of the orbital are of importance. Our finding of two almost identical transition densities ($U_1 \approx U_2$) does support Hagstrum's approach of deconvoluting the Auger spectrum in terms of a single transition density $U(\epsilon)$. The resulting transition density has a behavior that resembles the LDOS in a qualitative, yet not quantitative way.

Our present calculation contains approximations (mentioned in the Introduction) and they are limited to one particular system, He^+, outside a simple metal surface. In future calculations it would be important to improve on the approximations and also to consider a broader range of systems (we mention, e.g., electronegative atoms).

Ion neutralization spectroscopy is generally performed with the help of noble gas ions. Only for He the unoccupied ionic orbital is of s-wave character. For all other noble gas ions the unoccupied orbitals are of p type. The findings of Walkup *et al.*[5] that even the rate for an argon ion scales quadratically with the electron density, seems to indicate that the physics for neutralization into s- and p-type orbitals is about the same. This would support Hagstrum's conjecture that the matrix element effects in INS should be essentially independent of which type of ion is used. A thorough theoretical investigation of this fact would be interesting. The LDOS for the simple metal surfaces considered here is rather structureless, showing only a monotonic increase towards the higher energies. An investigation of to what extent the deconvoluted Auger spectrum ("transition densities") resembles the LDOS for a system showing more structure in its LDOS seems worthwhile.

Probably our most important approximation for the Auger rates is the neglect of the attractive potential of the positive He ion. In Refs. 20 and 9 these effects were estimated in simplified quasi-one-dimensional models. A proper inclusion of this effect would, however, require a full three-dimensional model. Then a computational framework, fundamentally different from the evaluation of the matrix element in the current work (see also Ref. 8) would have to be developed. For a direct comparison between experimental and theoretical Auger spectra also other effects such as the effects of the finite speed of the impinging ion and inelastic electron effects would have to be included. In addition, an inclusion of dielectric screening of the Coulomb interaction in the Auger matrix element should be considered.[21]

ACKNOWLEDGMENT

We wish to thank Professor B. I. Lundqvist for a critical reading of the manuscript.

[*] Present address: Institute of Physics, Estonian Academy of Sciences, 142 Riia Street, EE-2400 Tartu, Estonia.

[†] Present address: Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

[1] H. D. Hagstrum, Phys. Rev. **96**, 336 (1954).

[2] H. D. Hagstrum, Phys. Rev. **122**, 83 (1961).

[3] H. D. Hagstrum, Phys. Rev. **150**, 495 (1966). ,

[4] H. D. Hagstrum, in *Electron and Ion Spectroscopy of Solids*, edited by L. Fiermans, J. Vennik, and W. Dekeyser (Plenum, New York, 1978).

[5] R. E. Walkup, Ph. Avouris, N. D. Lang, and R. Kawai, Phys. Rev. Lett. **63**, 1972 (1989).

[6] M. W. Hart, M. S. Hammond, F. B. Dunning, and G. K. Walters, Phys. Rev. B **39**, 5488 (1989).

[7] J. A. Appelbaum and D. R. Hamann, Phys. Rev. B **12**, 5590 (1975).

[8] T. Fondén and A. Zwartkruis, Surf. Sci. **269/270**, 601 (1992).

[9] A. Zwartkruis and T. Fondén, Surf. Sci. **290**, 134 (1993).

[10] S. Horiguchi, K. Koyama, and Y. H. Ohtsuki, Phys. Status Solidi B **87**, 757 (1978).

[11] R. Hentschke, K. J. Snowdon, P. Hertel, and W. Heiland, Surf. Sci. **173**, 565 (1986).

[12] R. K. Janev and N. N. Nedeljković, J. Phys. B **18**, 915 (1985).

[13] C.-O. Almbladh and A. L. Morales, Phys. Rev. B **39**, 3503 (1989).

[14] L. A. Salmi, Phys. Rev. B **46**, 4180 (1992).

[15] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970).

[16] M. Alducin, A. Arnau, and P. M. Echenique, Nucl. Instrum. Methods B **67**, 157 (1992).

[17] N. Lorente and R. Monreal, Nucl. Instrum. Methods B **78**, 44 (1993).

[18] N. Lorente and R. Monreal (unpublished).

[19] W. Sesselmann, B. Woratschek, J. Küppers, G. Ertl, and H. Haberland, Phys. Rev. B **35**, 1547 (1987).

[20] D. R. Penn and P. Apell, Phys. Rev. B **41**, 3303 (1990).

[21] P. M. Echenique, F. Flores, and R. H. Ritchie, Solid State Phys. **43**, 229 (1990).