Role of target polarization
in the electron capture by ions in metals

R. Díez Muiño

Donostia International Physics Center (DIPC),
P. Manuel de Lardizabal 4, 20018 San Sebastián, Spain

Abstract

We review some of the theoretical approximations used to calculate Auger capture rates from the valence band of a free electron gas to the bound state of a static ion. The polarization created by the ion in the gas is accounted for and its effects in the Auger rate discussed. Many-body effects in the medium response are analyzed as well. We choose the neutralization of a He\(^+\) ion as a test case. We show that the results depend very much on the level of approximation used. We conclude that an accurate calculation of the Auger rate requires a refined description of the ion/gas system.

Key words: Auger processes, Screening, Density Functional Theory
PACS: 78.70.-g, 79.20.Rf, 73.90.+f

1 Introduction

Slow atomic particles interacting with metals (either at surfaces or in bulk) are screened by the medium electrons. The screening is provided by a rearrangement of electronic charge in the vicinity of the projectile. The polarization induced in the metal by the particle strongly depends on the particle charge state. In a typical interaction process, the charge state of the moving particle varies along its trajectory. Electron capture from the target to the ion reduces the charge state of the latter. One of such electron capture mechanisms is the Auger process, in which an electron jumps from the valence band of the metal to an ion bound state. The energy released in such transition is balanced by an electronic excitation in the medium. Other possible processes are resonant

\[1\] Phone: (+34)943015366, Fax: (+34)943015600, email: rdm@sc.ehu.es

Manuscript accepted in Nuclear Instruments and Methods B (October 25th 2002)
charge transfer and radiative capture, the latter only important for heavy ions. Electron loss from a bound state of the projectile to unoccupied states of the metal can happen as well. For slow ions, the competition between the capture and loss processes may eventually lead to a complete neutralization of the projectile. The time scale at which the neutralization process takes place is crucial to understand the experimental outputs provided by different spectroscopies.

The theoretical study of the Auger processes requires an accurate description of the ion/metal system. The strong perturbation introduced by a slow ion in a metal prevents the use of linear response theory to describe the screening process. Collective effects in the metal response are also important in many cases. Our purpose in this paper is to describe some theoretical models that we used in the past to calculate Auger rates and discuss the role of the different approximations involved in them. As a test case, we focus on the neutralization of a He$^+$ ion inside a metal bulk. The valence-band of the metal is represented in the following by a free electron gas (FEG). We restrict ourselves to a static approximation, which should remain valid for real systems in which the He$^+$ ion moves with a velocity smaller than the Fermi velocity of the medium electrons. We start with the theoretical description of the ion screening process in Section 2, and discuss the Auger capture processes in Section 3.

An additional motivation for the choice of He$^+$ as an example is its importance in several spectroscopical techniques. The neutralization of He$^+$ ions at surfaces is widely used as an experimental tool to study the electronic properties of solid surfaces since the pioneering work of Hagstrum [1]. Electron- [2-4] and ion-based [2,5-7] spectroscopies provide useful information on surface electronic excitations and charge transfer rates. Spin-dependent studies have been developed as well [8-11]. There has also been much theoretical work on the neutralization of He$^+$ ions at surfaces [12-16] and in bulk [17]. Some of these works use approximations discussed in this paper. Although our calculations are performed just in bulk, the results should help to understand the achievements and limitations of these approximations.

Atomic units are used throughout unless otherwise stated.

2 Density Functional Theory of Ion Screening in Metals

The dynamical screening of light ions in a FEG has been thoroughly studied using linear response theory [18]. Linear theory remains valid for $Z/v \ll 1$, with $Z$ the ion charge and $v$ its velocity. However, the strong perturbation introduced by a static ion in a FEG cannot be well represented in such an approximation and non-linear effects have to be accounted for. Density functional theory (DFT) provides an effective way to calculate the self-consistent
screening of an ion in a FEG [19,20]. The large piling-up of charge in the vicinity of the ion is calculated to all orders in the Z-perturbation series. We use Kohn-Sham (KS) equations [21]:

\[
\left\{-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r})\right\} \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})
\]

(1)

to obtain self-consistently the effective potential \(v_{\text{eff}}(\mathbf{r})\) and the electronic density \(\Delta n(\mathbf{r}) = n(\mathbf{r}) - n_0\) induced by an impurity \(Z\) embedded in a FEG of mean density \(n_0\) [20]. The effective potential \(v_{\text{eff}}(\mathbf{r})\) is composed of three terms, namely the external potential created by the external impurity \(v_{\text{ext}}(\mathbf{r}) = -Z/r\), the electrostatic potential \(v_{\text{es}}(\mathbf{r}) = \int d\mathbf{r}' \Delta n(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|\), and the exchange-correlation potential \(v_{\text{xc}}(\mathbf{r})\) calculated in the local density approximation (LDA) [22]. The electronic density is calculated as a sum over occupied orbitals \(n(\mathbf{r}) = \sum_{i\in\text{occ}} |\varphi_i(\mathbf{r})|^2\). The induced electronic density \(\Delta n(\mathbf{r})\) can be split into two terms \(\Delta n(\mathbf{r}) = \Delta n^b(\mathbf{r}) + \Delta n^c(\mathbf{r})\), one accounting for the contribution of the KS bound states \(\Delta n^b(\mathbf{r})\), and a second one accounting for the contribution of the scattering states \(\Delta n^c(\mathbf{r})\) [23].

We perform a DFT calculation of the He\(^+\) ion embedded in a FEG by solving iteratively the set of equations Eq. (1) with \(Z = 2\), and populating just one of the two bound KS orbitals. The screening of the hole thus created is provided by the electronic charge induced in the continuum \(\Delta n^c(\mathbf{r})\), which integrates to the unit charge. Fig. 1(a) shows the 1s KS orbital of the He\(^+\) ion embedded in a FEG of \(r_s = 3\) (\(r_s\) is defined from \(n_0 = 3/\pi r_s^3\)). The shape of the 1s KS orbital is very similar to a Hartree-Fock-Slater (HFS) description of the 1s orbital of He 1s\(^1\)2s\(^1\) in the gas phase. We also plot in Fig. 1(b) the DFT calculation of the electronic density induced in the continuum \(\Delta n^c(\mathbf{r})\) by a He\(^+\) ion embedded in a FEG of \(r_s = 3\). The result is compared to the HFS calculation of the electronic density of the 2s electron in atomic He 1s\(^1\)2s\(^1\). Previous calculations of the screening of highly-charged ions in metals showed that the shape of the electronic charge induced in the continuum has an atomic-like character and resembles the spatial distribution of electronic charge in the excited states of gas-phase atoms [24]. This is not the case in the embedding of the He\(^+\) ion. Although the position of the first two peaks in Fig. 1(b) is quite similar, the shape of the electronic density clouds differ. The density induced in the continuum \(\Delta n^c(\mathbf{r})\) contains much more structure and presents wide Friedel oscillations at long distances.

The deviation of \(\Delta n^c(\mathbf{r})\) from an atomic-like character is better understood with the help of an auxiliary quantity, namely the density of levels induced by the impurity in the continuum \(\delta \rho(k)\) [23]:

\[
\delta \rho(k) = \frac{2}{\pi} \sum_l (2l + 1) \frac{d}{dk} \delta \tilde{\gamma}(k)
\]

(2)
where \( k \) is the electron momentum \((\varepsilon = k^2/2)\), \( l \) is the angular momentum in a partial-wave expansion, and \( \delta_l(k) \) are the phase shifts of the KS radial wavefunctions.

Figure 2 shows \( \delta \rho(k) \) as a function of \( k \) for several values of \( r_s \). There is a resonance peak at low densities (high \( r_s \)) that progressively disappears as the medium electronic density increases. This resonance is originated by the coupling between the He atomic states and the FEG continuum. When the resonance has a well-defined partial-wave symmetry, it can be associated with a single electronic state in the gas-phase atom. However, and in the case of He\(^+\), there is no clear connection between the resonance and one single atomic state: the resonance is basically composed of both s- \((l = 0)\) and p- \((l = 1)\) scattering states and cannot be assigned to a single partial-wave symmetry. For this reason, the spatial distribution of the induced electronic density is different from that of the 2s electron in He 1s\(^1\)2s\(^1\).

The theoretical calculation of the Auger rates discussed in Section 3 requires an accurate description of the one-electron wavefunctions involved in the decay process. The KS states obtained by the procedure explained above provide a good approximation to such wavefunctions and can be used as a direct input for the calculation of Auger rates.

### 3 Auger Processes of Electron Capture

In an Auger capture process, an electron decays from a metal valence band state \(| \varphi_1 \rangle \) of energy \( \varepsilon_1 = k_1^2/2 \) to a bound state of the ion \(| \varphi_a \rangle \) of energy \( \varepsilon_a \). An individual (electron-hole pair) or collective (plasmon-type) excitation of energy \( \omega = \varepsilon_1 - \varepsilon_a \) is created at the same time in the metal. The Auger process thus modifies the charge state of the ion. Our description implicitly assumes that one of the electrons of the medium (the one that is captured) can be distinguished from the rest. The process is schematically shown in Fig. 3.

In the self-energy formalism, the Auger capture probability per unit time \( \Gamma \) can be calculated in terms of the screened Coulomb interaction \( W(r, r', \omega) \) [25]:

\[
\Gamma = -2 \sum_{\varphi_1 \in \text{occ.}} \text{Im} \left\{ \int dr dr' \varphi^*_a(r) \varphi^*_1(r') W(r, r', \omega = \varepsilon_1 - \varepsilon_a) \varphi_a(r') \varphi_1(r) \right\}
\]

(3)

where \( \text{Im} \{x\} \) denotes imaginary part of the complex number \( x \), and the sum over occupied states \( \varphi_1 \) includes all scattering states with energies from the
bottom of the band $\varepsilon_1 = 0$ to the Fermi level $\varepsilon_F = k_F^2/2$. The screened interaction $W(r, r', \omega)$ can be calculated in terms of the many-body response function of the system $\chi(r, r', \omega)$ and the bare Coulomb potential $v(r, r') = 1/|r - r'|$:

$$
W(r, r', \omega) = v(r, r') + \int dr_1 dr_2 \, v(r, r_1) \, \chi(r_1, r_2, \omega) \, v(r_2, r') \ .
$$

(4)

The imaginary part of the response function $\chi(r, r', \omega)$ is related to the probability of creating excitations in the medium. Different descriptions of the electronic excitations result in different descriptions of the response function $\chi(r, r', \omega)$. The simplest approximation is to remain at the so-called Hartree level, in which the electronic excitations in the medium are described in the independent-particle approximation. The response function in this approximation $\chi_0(r, r', \omega)$ can be calculated in real space as a sum over single-particle electronic wavefunctions $\varphi_2(r)$ and $\varphi_3(r)$ (with energies $\varepsilon_2$ and $\varepsilon_3$) [26]:

$$
\chi_0(r, r', \omega) = \sum_{\varphi_2 \in \text{occ.}} \sum_{\varphi_3 \not\in \text{occ.}} \left[ \frac{\varphi_3^*(r)\varphi_2^*(r')\varphi_3(r)}{\omega + \varepsilon_2 - \varepsilon_3 + i\delta} - \frac{\varphi_3^*(r)\varphi_2^*(r')\varphi_3(r)\varphi_2^*(r)}{\omega - \varepsilon_2 + \varepsilon_3 + i\delta} \right],
$$

(5)

where the sum over $\varphi_2$ ($\varphi_3$) runs over occupied (unoccupied) scattering states, and $\delta$ is a positive infinitesimal. In practice, the sum over final states can be simplified with the help of one-electron Green functions $G(r, r', \omega)$ [27]. It can be shown that the calculation of $\text{Im} [\chi_0]$ in real space and its subsequent substitution in the expressions for the Auger rate, Eqs. (3) and (4), leads to the standard Fermi's golden rule for the calculation of the Auger rate in the independent-particle approximation [28]:

$$
\Gamma = 2\pi \sum_{\varphi_1 \in \text{occ.}} \sum_{\varphi_2 \in \text{occ.}} \sum_{\varphi_3 \not\in \text{occ.}} \left| \int dr dr' \, \varphi_1^*(r)\varphi_3^*(r')v(r, r')\varphi_2(r')\varphi_2^*(r) \right|^2 \\
\times \delta (\varepsilon_1 + \varepsilon_2 - \varepsilon_\alpha - \varepsilon_3) .
$$

(6)

The independent-particle response function $\chi_0$ can be used as well as an input to calculate self-consistently the many-body response function of the interacting-electron system $\chi$, [25]. The latter includes collective excitations, that may be important for a certain range of energies. For the unperturbed FEG, the calculation of $\chi$ in the random-phase approximation (RPA) leads to the Lindhard function [29] or some modifications of it, such as the Mermin function [30]. The Lindhard function is equivalent to the use of plane waves as one-electron wavefunctions in Eq. (5), before the self-consistent calculation of $\chi$. The calculation of the Auger rate $\Gamma$ using these functions is usually
simplified by working in Fourier space [18]:

$$\Gamma = \frac{4}{\pi} \sum_{\varphi_1, \varphi_\alpha} \int \frac{d^3q}{q^3} \left| \int d^3r \varphi_\alpha(r)e^{iqr}\varphi_1(r) \right|^2 \text{Im} [\chi(q, \omega = \varepsilon_1 - \varepsilon_\alpha)] . \quad (7)$$

We show in the following that the theoretical calculation of $\Gamma$ depends very much on the level of approximation used to describe (i) the wavefunctions $\varphi_\alpha(r)$ and $\varphi_1(r)$, and (ii) the screened interaction $W(r, r', \omega)$ [or, equivalently, the response function of the system $\chi(r, r', \omega)$].

### 3.1 Wavefunctions in the decay process

In order to show the effect that a proper description of the initial and final state wavefunctions $\varphi_1(r)$ and $\varphi_\alpha(r)$ has in the calculation of the Auger rate, we calculate the neutralization rate of a He$^+$ ion in a FEG of $r_s = 2$. The final wavefunction in the decay process is calculated as a hydrogenic wavefunction with an effective charge $Z_e$, i.e., $\varphi_\alpha(r) = (Z_e^3/\pi)^{1/2} e^{-Z_e r}$. As we want to show the effect of varying just the wavefunctions, we keep a constant value of the bound state energy $\varepsilon_\alpha \approx -0.15$ a.u. (as used for instance in Ref. [15]) in the calculation of the transition energy $\omega$. The screened interaction $W(r, r', \omega)$ is that of the unperturbed FEG in the RPA: We work in Fourier space and use a Mermin-type response function [30] in Eq. (7).

We plot in Fig. 4 the theoretical calculation of the Auger capture rate as a function of the effective charge $Z_e$ using different approximations to calculate the initial state wavefunctions $\varphi_1(r)$: (i) plane waves (denoted as PW in the plot), (ii) plane waves orthogonalized to the final wavefunction $\varphi_\alpha(r)$ (OPW), (iii) Coulomb wavefunctions defined from the same effective charge $Z_e$ (CW), and (iv) KS states, numerical solutions of the DFT He$^+/r_s = 2$ system, orthogonalized to $\varphi_\alpha(r)$ (KS). The Auger rate calculated using KS states both for $\varphi_1(r)$ and $\varphi_\alpha(r)$ is plotted as well (KS-KS) as a flat line. In this latter case, the KS $\varphi_\alpha(r)$ orbital is calculated numerically and obviously does not have any dependence on $Z_e$. The KS-KS calculation is the most sophisticated one and is plotted as a reference to check the accuracy of the other models.

The effective charge $Z_e$ measures the spatial extension of the final wavefunction $\varphi_\alpha(r)$ in the Auger decay process. Figure 4 shows that $\Gamma$ varies very much when running from $Z_e = 1$ to $Z_e = 2$ for the same description of the initial wavefunction $\varphi_1(r)$. A careful choice of the final wavefunction $\varphi_\alpha(r)$ shows to be crucial in the calculation of the Auger rate. Furthermore, Fig. 4 shows that the choice of the initial wavefunction $\varphi_1(r)$ in the process is important as well: the value of $\Gamma$ varies orders of magnitude when passing from one theoretical description to another. For an accurate calculation of $\Gamma$, the initial wavefunc-
tions \( \varphi_1(\mathbf{r}) \) should gather the following properties: (i) to be orthogonal to \( \varphi_\alpha(\mathbf{r}) \), and (ii) to include the ion perturbation at least in an approximate way.

3.2 Medium response in the decay process

An additional ingredient that enters the calculation of the Auger rate is the description of the electronic excitations created in the medium. The piling-up of charge introduced by the ion in the target, already shown to be important in the calculation of the wavefunctions, can also be included in the calculation of the response function by using KS states in Eq. (5). For strong perturbations of the target (highly charged ions, for instance), the latter inclusion can change as much as one order of magnitude the value of the Auger rate [28]. The effect is smaller for He\(^+\), as shown in Fig. 5, in which we plot the theoretical calculation of the Auger capture rate \( \Gamma \) for a He\(^+\) ion in a FEG as a function of \( r_s \). The wavefunctions \( \varphi_\alpha(\mathbf{r}) \) and \( \varphi_1(\mathbf{r}) \) are represented by KS states. Three different response functions are used: (i) the independent-particle \( \chi_0 \) of the unperturbed FEG (built from plane waves), (ii) the independent-particle \( \chi_0 \) of the FEG perturbed by the ion (built from KS states), and (iii) the many-body response function \( \chi \) of the unperturbed FEG (Mermin function). Calculations (i) and (ii) are performed in real space, and calculation (iii) is performed in Fourier space. The difference between (i) and (ii) shows the effect of including the target modification in the calculation of the response function. The difference between (i) and (iii) shows the importance of including many-body effects in the medium response. The Auger rate approximately scales as \( \Gamma \propto n_0^{1.74} \) in (ii) and \( \Gamma \propto n_0^{1.82} \) in (iii). This scaling, close to \( n_0^2 \), is a consequence of the double sum over occupied states that appears in Eq. (6). The sum is implicit in the other expressions to calculate the Auger rate. However, the medium polarization is larger for ions of higher charge and the density dependence is weaker [31].

The comparison between the three different models for the calculation of the response function is also analyzed in Fig. 6, in which the differential Auger rate \( d\Gamma/d\varepsilon_1 \) (defined in such a way that \( \Gamma = \int_0^\infty [d\varepsilon_1 \left( d\Gamma/d\varepsilon_1 \right)] \)) is shown as a function of the initial energy in the decay process \( \varepsilon_1 \). The three different panels correspond to three different values of \( r_s \). The upper panel shows the case of \( r_s = 1.5 \), in which the energy threshold for plasmon excitation is situated at \( \varepsilon_1 \approx 0.37 \). Plasmons are a distinctive feature of many-body effects. Only a self-consistent calculation of the response function, such as that performed with the Mermin response function \( \chi \), is capable of including them. A clear structure caused by the sudden appearance of the plasmon can be seen in the plot. A similar result was obtained by Lorente et al. for He\(^+\) ions at surfaces [14]. For the two other values of \( r_s \) (\( r_s = 2 \) and \( r_s = 3 \)), the threshold for plasmon excitation is below the bottom of the band and no plasmon structure

7
is found.

The Auger rates calculated here can be compared with theoretical results obtained for the neutralization of He\(^+\) at metal surfaces, such as those of Cazalilla \textit{et al.} [15]. Reference [15] shows a bulk limit for the Auger rate of He\(^+\) at an Al surface of the same order of magnitude as ours [i.e., \(O(10^{-2})\) a.u. for \(r_s = 2\)], although smaller. The small discrepancy is due to differences in the description of the wavefunctions involved in the process \(\varphi_0(\mathbf{r})\) and \(\varphi_1(\mathbf{r})\), as well as in the value of the transition energy \(\omega\). Nevertheless, information extracted from Ref. [15] and from the present work can be combined to estimate the distance-dependent Auger rates for He\(^+\) ions at surfaces other than Al.

4 Conclusions

We have shown that the strong perturbation introduced by a He\(^+\) ion in a FEG has to be accounted for in the theoretical calculation of the Auger neutralization rates. The ion perturbation modifies both the one-electron wavefunctions required to calculate the matrix element in the decay process \([\varphi_0(\mathbf{r})\) and \(\varphi_1(\mathbf{r})]\) and the medium response to such a decay. We have shown that a DFT calculation of the He\(^+\) ion embedded in a FEG provides KS wavefunctions that are useful to account for the ion perturbation in both senses. So far, the inclusion of the ion perturbation in the calculation of the medium response has been only performed in the independent-particle approximation. The obvious improvement that still remains to be done is the calculation of the self-consistent response function \(\chi\) of the ion/FEG system. Work along this line is currently in progress.

5 Acknowledgements

Scientific collaboration with A. Arnau, M. A. Cazalilla, S. A. Deutscher, P. M. Echenique, A. Salin, and E. Zaremba is gratefully acknowledged. This work was supported in part by the Basque Departamento de Educación, Universidades e Investigación, the University of the Basque Country UPV/EHU (9/UPV 00206.215-13639/2001), and the Spanish Ministerio de Ciencia y Tecnología (MAT2001-0946). Financial support by the Gipuzkoako Foru Aldundia (Gipuzkoa Fellows Program) is acknowledged as well.
References


Fig. 1. (a) Radial electronic density $4\pi r^2 \Delta n^b(r)$ of the 1s KS orbital for a He$^+$ ion embedded in a FEG of $r_s = 3$, as calculated in DFT (solid line). The dotted line shows the radial electronic density of the 1s atomic orbital of He $1s^12s^1$ in the gas phase, as calculated in the HFS approximation. (b) Radial electronic density $4\pi r^2 \Delta n^c(r)$ induced in the continuum by a He$^+$ ion embedded in a FEG of $r_s = 3$, as calculated in DFT (solid line). The dotted line shows the radial electronic density of the 2s atomic orbital of He $1s^12s^1$ in the gas phase, as calculated in the HFS approximation. Densities are plotted as a function of the radial coordinate $r$. All quantities in atomic units.
The energy of the excitation in the medium, the energy of the excitation in an electron-hole pair or a collective excitation, is created at the same time in the electron and the energy of an electronic excitation (other than the states related to the X-ray absorption). The energy in a state in the valence band, to a bound state of the ion |2⟩ |2⟩ is added to the energy capture process. An electron decays from the excited state of the radiation into the ground state of the atom |1⟩ |1⟩.

Figure 2. Schematic drawing of the energy capture process. An electron decays from the excited state of the radiation into the ground state of the atom |1⟩ |1⟩.

Figure 3. Density of levels ρ(ε) induced in the continuum of a He-like [He]...
Fig. 4. Theoretical calculation of the Auger capture rate $\Gamma$ for a He$^+$ ion in a FEG of $r_s = 2$ as a function of the effective charge $Z_e$. The initial state wavefunctions $\varphi_1(r)$ are calculated using different approximations: the solid line shows the result of using plane waves (PW), the dashed line of using plane waves orthogonalized to the final state wavefunction (OPW), the dotted line of using Coulomb wavefunctions (CW), and the dash-dotted line of using Kohn-Sham states orthogonalized to the final state wavefunction (KS). The Auger rate calculated using KS states both for the initial and final wavefunctions is plotted as well as a flat thin-dotted line (KS-KS). All quantities in atomic units.

Fig. 5. Theoretical calculation of the Auger capture rate $\Gamma$ for a He$^+$ ion in a FEG as a function of $r_s$. The wavefunctions in the decay process $\varphi_1(r)$ and $\varphi_2(r)$ are calculated using KS states. Three different approximations are used in the calculation of the response function: the independent-particle response function $\chi_0$ of the unperturbed FEG (dashed line), the independent-particle response function $\chi_0$ of the FEG perturbed by the He$^+$ ion (dotted line), and the many-body response function $\chi$ of the unperturbed FEG (solid line). All quantities in atomic units.
Fig. 6. Theoretical calculation of the differential Auger capture rate $d\Gamma/d\varepsilon_1$ for a He$^+$ ion in a FEG as a function of the initial energy of the decaying electron $\varepsilon_1$. The different approximations used in the calculation of the response function are those of Fig. 5. The line styles follow the same convention as well. The upper panel shows the case $r_s = 1.5$, the middle panel shows $r_s = 2$, and the lower panel $r_s = 3$. All quantities in atomic units.