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ATTRACTIVE POTENTIALS FOR HELIUM ATOMS AT INTERMEDIATE DISTANCES FROM THE METAL SURFACE THE ROLE OF THE ATOMIC MATRIX ELEMENTS

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Attractive electrostatic potential between a helium atom and the jellium surface is studied using the non-local dynamically screened Coulomb interaction which describes the electronic (single particle and collective) fluctuations in the metal. It is shown that the detailed form of the atomic matrix elements and the higher multipole contributions lead to the strong modification of the van der Waals attraction even when one neglects the dispersion and damping of the electronic excitations in the metal. Therefore it becomes necessary to treat both the atomic and the metallic effects within the same accuracy.

1. Introduction

In this paper we study the attractive potential acting on a neutral particle close to the metallic surface, due to its interaction with the electronic excitations in the metal. The theory is based on a recent approach in terms of the self-consistent non-local dynamical potential near a metallic surface$^{1)}$.

After establishing the connection with the usual *classical* van der Waals potential in its somewhat generalized form, we briefly discuss the quantum mechanical corrections, arising from the spatial extension of the electronic fluctuations on the atom, and from the dispersive properties of the fluctuations in the metal, as well as the dynamical corrections.

We apply these results to calculate the attractive potential for the helium atom in front of a planar metal (jellium) surface, illustrating in particular the role of the nonlocality of the potential and spatial dependence of the atomic electronic orbitals.

2. *Formulation of the problem*

The interaction of the external particle with the electronic excitations in the metal can be described by means of the dynamically screened non-local potential[1] between the points $\vec{r} = (\vec{\varrho}, z)$ and $\vec{r}' = (\vec{\varrho}', z')$ outside the metal surface $(z, z' > 0)$:

$$W(\vec{r}, \vec{r}', \omega) = \int \frac{\mathrm{d}\vec{Q}}{(2\pi)^2} \mathrm{e}^{i\vec{Q}(\vec{\varrho}-\vec{\varrho}')} W(Q, z, z', \omega)$$

where $$W(Q, z, z', \omega) = v_Q \, \mathrm{e}^{-Q(z+z')} D(Q, \omega), \quad v_Q = \frac{2\pi \mathrm{e}^2}{Q}$$

are its Fourier components, and $\vec{Q}$ is a two dimensional wavevector parallel to the surface (Fig. 1). $D(Q, \omega)$ is the propagator of the electronic excitations in the metal, which can be spectrally decomposed[2]:

$$D(Q, \omega) = \int_0^\infty \mathrm{d}\omega' \, S(Q, \omega') \left(\frac{1}{\omega + \omega' - \mathrm{i}\eta} - \frac{1}{\omega - \omega' + \mathrm{i}\eta} \right)$$

and describes the induced non-retarded Coulomb coupling between the charges outside the metal via the electronic fluctuations in the metal.

The classical image potential corresponds to the shift in the ground state energy of the total system (metal plus external charge) due to the charge coupling with the electronic excitations. The van der Waals (or dispersion) potential is the energy shift that arises from the coupling of the excitations on the particle and in the metal, and has, strictly speaking, no classical counterpart. For an electronic transition, $|0\rangle \to |i\rangle$, on the particle, this process can be represented, in the lowest order, by the vacuum fluctuation diagram, shown in Fig. 2. In particular, the generalized van der Waals potential is due to the virtual excitation of the dipolar (e. g. $1s \to 2p$) and higher order transitions on the atom. We shall restrict ourselves to this lowest order diagram, and neglect all higher terms (chain diagrams, bubble renormalization, etc.)

The calculation of this diagram using modified Feynman rules[2] leads to the expression:

$$\Sigma(\omega_i, R) = -\mathrm{i} \int \frac{\mathrm{d}\vec{Q}}{(2\pi)^2} v_Q \, |M_i(\vec{Q}, R)|^2 \int_0^\infty \mathrm{d}\omega \frac{S(Q, \omega)}{\omega_i + \omega + \mathrm{i}\,\eta}. \tag{1}$$

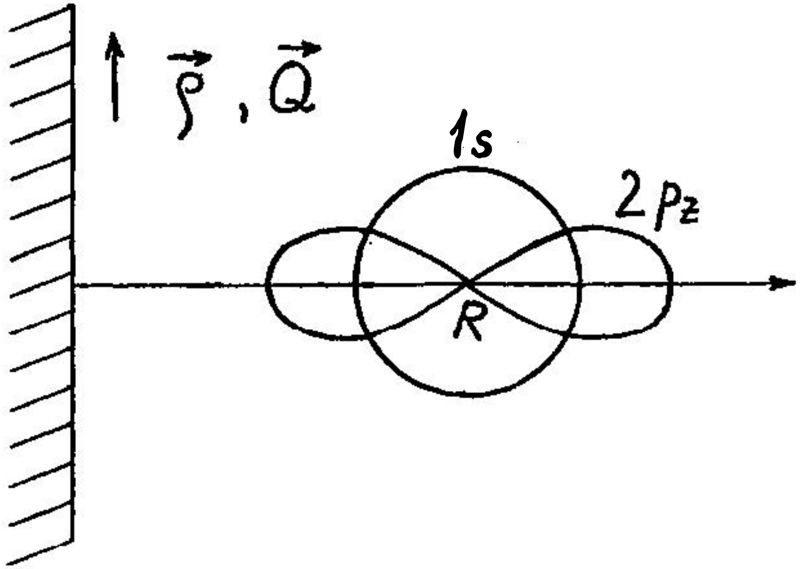

Fig. 1. The geometry of the system with two atomic orbitals ($1s$ and $2p_z$) shown schematically.

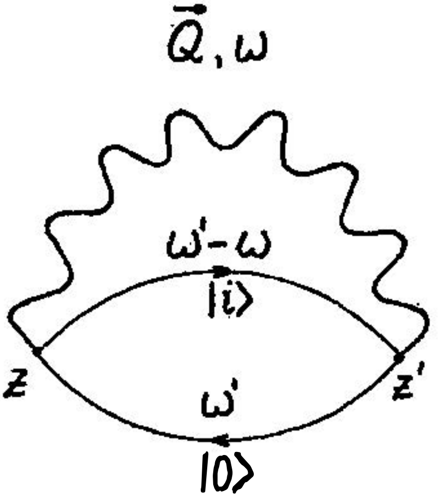

Fig. 2. The second order vacuum polarization Feynman diagram for the van der Waals potential energy.

Here the index i denotes a particular atomic transition $|0\rangle \rightarrow |i\rangle$, and M_i are the matrix elements:

$$M_i(\vec{Q}, R) = \langle i \,|\, e^{-Qz}\, e^{i\vec{Q}\vec{\rho}}\, |0\rangle$$

taken between the atomic wavefunctions centred at the distance R from the surface.

The real part of (1) gives the energy shift of the system, which is the R-dependent van der Waals potential energy for a particular electronic transition:

$$\Delta E_i(R) = -\int_0^\infty \frac{Q\,\mathrm{d}Q}{2\pi} v_Q \widetilde{M}_i^2 \int_0^\infty \mathrm{d}\omega \frac{S(Q,\omega)}{\omega_i + \omega} \tag{2}$$

where

$$\overline{|M_i(\vec{Q},R)|^2} \equiv \widetilde{M}_i^2 = \frac{1}{2\pi}\int_0^\infty \mathrm{d}\varphi\, |M_i(\vec{Q},R)|^2.$$

The total van der Waals potential energy is the sum of the contributions due to all possible electronic transitions $|0\rangle \to |i\rangle$ on the atom, as weighted by the matrix elements $\widetilde{M}_i$, including the energy denominators in (2). Similarly, the weights of the electronic transitions in the solid are given by $S(Q,\omega)$ for each wavevector $\vec{Q}$.

3. *Calculation for the helium*

In the helium atom we shall consider the following transition:

$$1s^2 \to 1s'\,2p \qquad \Delta E = 20.96\ \mathrm{eV}$$

where $1s'$ is the state of the $1s$ electron exposed to the full nuclear charge $2e$. The radial wave functions are taken to be the Slater functions:

$$R_{nl} \sim r^{n^*-1}\,\mathrm{e}^{-\zeta_{nl}\,r/n^*a_0}$$

with the Clementi-Raimondi parameters (Appendix 1). The orthonormalized wave functions ψ_{nl} are also given in Appendix 1.

The matrix elements M_i are calculated for the transitions:

$$1s^2 \to 1s'\,2p_z \qquad M_z$$

$$1s^2 \to \begin{cases} 1s'\,2p_x & M_x \\ 1s'\,2p_y & M_y \end{cases} \qquad \widetilde{M}_x = \widetilde{M}_y$$

and are given in Appendix 2.

It is convenient to separate the matrix elements into:

$$\widetilde{M}_i^2 = Q^2\,\mathrm{e}^{-2QR}\,p_i^2\,m_i(Q,R) \qquad (i = \|, z). \tag{3}$$

In the above formula we introduced the quantities

$$\widetilde{M}_{\|}^2 = \widetilde{M}_x^2 + \widetilde{M}_y^2; \qquad 2p_{\|}^2 = p_x^2 + p_y^2$$

where

$$p_j = \lim_{R \to \infty} \langle 2p_j | r_j | 1s \rangle \qquad (j = x, y, z)$$

is the asymptotic dipole matrix element.

Our calculation gives the asymptotic value

$$p_j = 0.0131 \text{ nm}$$

which, in view of the simplicity of the model, is in reasonable agreement with the one obtained from the oscillator strength of the transition $1s \to 2p$:

$$\langle 2p_z | z | 1s \rangle = 0.0178 \text{ nm.}$$

The $Q^2 e^{-2QR} p_i^2$ part leads to the well-known R^{-3} van der Waals potential in the case of $1s \to 2p_{x,y}$ and $1s \to 2p_z$ transitions, while $m_i (Q, R)$ gives the quantum mechanical modulation due to the finite extent of the electronic orbitals that participate in the transition. It must be emphasized that this effect is not equivalent to averaging the local potential, i. e. the e^{-2QR} term, over the atomic orbitals.

The second source of corrections to the *classical* result comes from $S(Q, \omega)$ which contains the dispersion effects in its Q-dependence, as will be discussed in more detail in Ref. 3.

4. *The long wavelength limit*

The long wavelength limit $Q \to 0$ is obtained with[2)]

$$S(Q, \omega) \to \frac{\omega_s}{2} \delta(\omega - \omega_s)$$

where $\omega_s = \omega_p / \sqrt{2}$ is the asymptotic surface plasmon frequency. The dynamical effects would arise from the frequency denominator $\omega + \omega_i \to \omega_s + \omega_i$. For the perfect conductor ($\omega_p \to \infty$), when $R \to \infty$, ($m_i \to 1$), we obtain:

$$\Delta E_i = -\frac{e^2}{8R^3} p_i^2 \qquad (i = \|, z) \tag{4}$$

and find for the total van der Waals potential energy:

$$\Delta E(R) = -\frac{e^2}{16R^3} (p_x^2 + p_y^2 + 2p_z^2). \tag{5}$$

This is in agreement with the *classical* result[4)] for the dispersion forces, obtained in the framework of classical electrodynamics, with an ad hoc assumption about the coupling of the fluctuating dynamical dipoles. This should not obscure (as it often does) the fact that the van der Waals force is an essentially quantum mechanical phenomenon.

5. *The role of atomic matrix elements — discussion of results*

Now we discuss the deviations from the classical van der Waals force due to the variation of the normalized matrix elements m_i in (3) and (2).

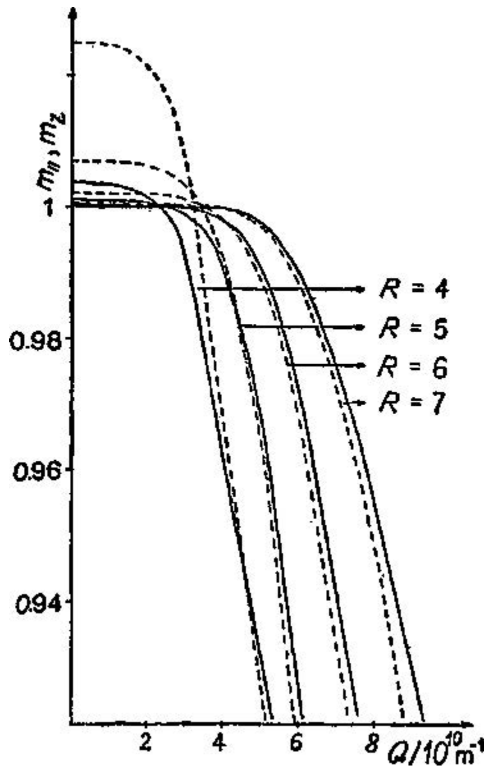

Fig. 3. The normalized matrix elements $m_{\|}(Q, R)$ (full line) and $m_z(Q, R)$ (dashed line) as functions of the wavevector $\vec{Q}$ for several distances R, which is expressed in 10^{-10} m.

Fig. 3 shows the Q-dependence of $m_{\|}$ and m_z for several distances R. For $Q \to 0$ both $m_{\|}$ and m_z tend to the asymptotic value 1, except at very short distances, where we find small (2—3%) deviations. These are due the form of our wavefunctions (Appendix 1) which are defined only outside the plane $z = 0$ and therefore describe the electrons which are *expelled* from the repulsive surface region.

Though this is by no means a valid description of the effect of the repulsive exchange and correlation potential in the electronic overlap region, nevertheless it leads to reasonable physical results, namely, the effective dipole matrix element $p_z(R)$ from its asymptotic (gas phase) value when we approach the surface. The effect is markedly lower for the parallel fluctuation $1s \to 2p_{x,y}$, i. e. in $m_{||}(Q, R)$.

This effect is also visible in Figs. 4a and 4b, which show the R-dependence of the normalized matrix elements for various values of the wavevector $\vec{Q}$, and especially in Fig. 4b, where it leads to enormous increase of m_z in the region very close to the surface ($R < a_0$), where our treatment is not justified and which should be excluded anyway.

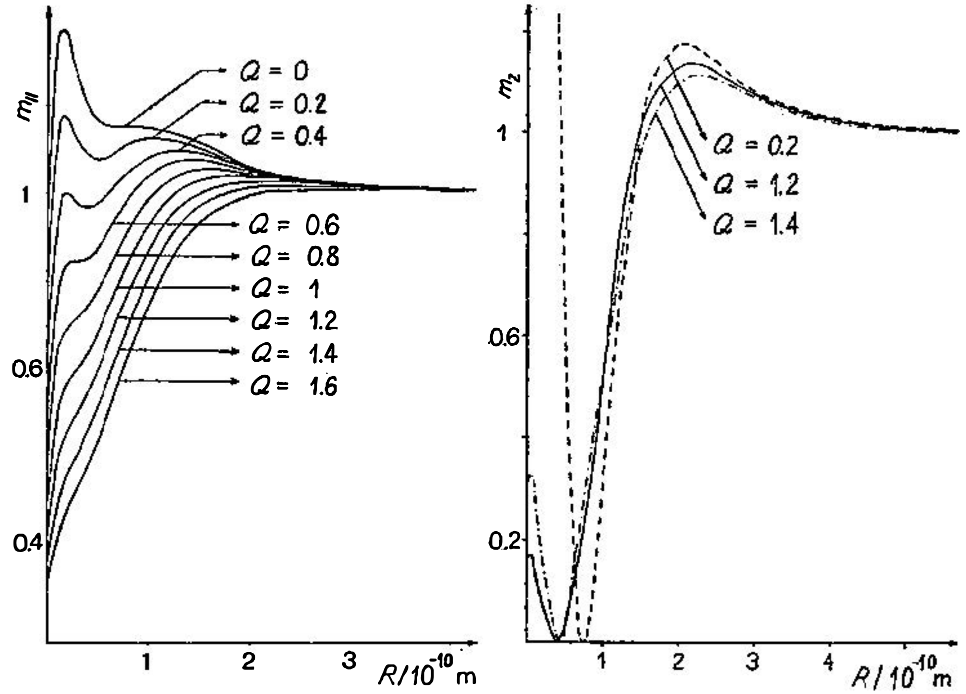

Fig. 4. The normalized matrix elements $m_{||}(Q, R)$ (Fig. 4a) and $m_z(Q, R)$ (Fig. 4b) as functions of R for several values of the wavevector $\vec{Q}$, which is expressed in 10^{10} m^{-1}.

The effect of nonlocality is given by the deviation of the normalized matrix elements $m_{||}$ and m_z from unity, as is obvious in Fig. 3 for higher values of the wavevector $\vec{Q}$, or in Fig. 4 as the helium position R approaches the surface. The detailed shapes and finite sizes of the electronic orbitals lead to the strong reduction in the coupling at shorter wavelengths. However, this effect has to be compared with the similar one due to the cutoff function e^{-2QR} in (4) and to the Q-dependence arising from the dispersion of the electronic excitations in the metal, as given by $S(Q, \omega)$.

Therefore, in order to estimate their overall importance for the van der Waals potential, we have to calculate (2). In this paper we shall study separately the matrix element corrections from the ones contained in $S(Q, \omega)$ and leave the full calculation to the later publication[3]. We therefore take the $Q \rightarrow 0$ limit in $S(Q, \omega)$. Then (2) becomes:

$$\Delta E_l(R) = -e^2 p_l^2 \frac{1}{2} \left(\frac{\omega_s}{\omega_s + \omega_l} \right) \int_0^\infty Q^2 \mathrm{e}^{-2QR} m_l(Q, R) \, \mathrm{d}Q. \qquad (6)$$

The result is shown in Fig. 5, for a helium atom and the jellium model of the metal, with the density and the surface plasmon frequencies corresponding to aluminium ($r_s = 2.074$, $\hbar \omega_s = 15.3/\sqrt{2}$ eV). The metal properties enter only through the prefactor $(1 + \omega_l/\omega_s)^{-1}$ and can be scaled out.

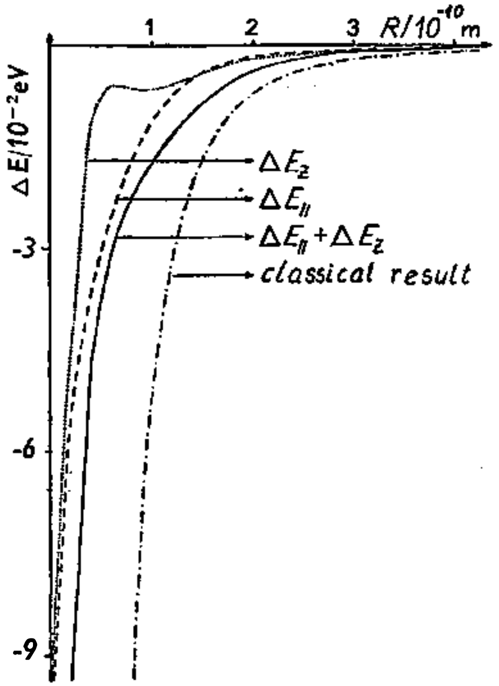

Fig. 5. Contributions to the van der Waals energy of a helium atom as a function of its distance R from jellium surface, with the aluminium density ($r_s = 2.074$, $\hbar \omega_s = 15.3/\sqrt{2}$ eV).

We notice a strong deviation from the *classical* result (5) even at relatively large distances. Our theory is strictly valid for $R > 3a_0 \approx 0.15$ nm, which is the size of the helium 2-p orbital, because we have neglected short-range exchange and correlation. At lower R we notice a small kink in $\Delta E_z(R)$ which — as discussed earlier — results from the additional polarization of He in our simple model, but this is already in the region where other effects should also be taken into account.

As expected, at intermediate distances ΔE_z gives a slightly larger contributions than $\Delta E_{||}$.

In conclusion, in the above calculations we have shown that the shape of the atomic matrix elements m_l strongly influences the van der Waals potential energy of the helium atom at intermediate distances from the metal surface, e. g. between 0.15 nm and 0.5—0.6 nm, where the long-range electrostatic forces dominate.

The final result obviously has to take into account the detailed knowledge of the long-range electronic excitations in the solid[5, 6, 7], as will be done elsewhere[3], but even this partial calculation shows that it is necessary to treat both systems of electronic excitations — metallic and atomic — within the same degreee of accuracy.

Appendix 1. *The wave functions*

1*s-state*

$n^* = 1$

$\zeta_{1s} = 1.6875$

$\alpha_1 = 1.6875/a_0$

$$\Psi_{1s} = \frac{1}{N_{1s}} \mathrm{e}^{-\alpha_1 \sqrt{\varrho^2 + (z-R)^2}}$$

$$N_{1s}^2 = \frac{\pi}{\alpha_1^3} \left[1 - \frac{1}{2} (1 + \alpha_1 R) \, \mathrm{e}^{-2\alpha_1 R} \right]$$

1*s*′*-state*

$n^* = 1$

$\zeta_{1s'} = 2$

$\alpha'_1 = 2/a_0$

$$\Psi_{1s'} = \frac{1}{N_{1s'}} \mathrm{e}^{-\alpha'_1 \sqrt{\varrho^2 + (z-R)^2}}$$

$$N_{1s'}^2 = \frac{\pi}{\alpha'^3_1} \left[1 - \frac{1}{2} (1 + \alpha'_1 R) \, \mathrm{e}^{-2\alpha'_1 R} \right].$$

2*p-states*

$n^* = 2, \; \zeta_{2p} = 1, \; \alpha_2 = 1/a_0$

$$\Psi_{2p_j} = \frac{1}{N_{2p_j}} \begin{Bmatrix} \varrho \cos \varphi \\ \varrho \sin \varphi \\ z - R \end{Bmatrix} \mathrm{e}^{-\frac{\alpha_2}{2} \sqrt{\varrho^2 + (z-R)^2}} \qquad j = x, y, z$$

$$N_{2p_x}^2 = N_{2p_y}^2 = \frac{2\pi}{\alpha_2^5} \left[16 - (8 + 5\alpha_2 R + \alpha_2^2 R^2) \, \mathrm{e}^{-\alpha_2 R} \right]$$

$$N_{2p_z}^2 = \frac{2\pi}{\alpha_2^5} \left[16 - (8 + 8\alpha_2 R + 4\alpha_2^2 R^2 + \alpha_2^3 R^3) \, \mathrm{e}^{-\alpha_2 R} \right].$$

Appendix 2. *The matrix elements* (3)

$$M_{\|} = 2\pi \frac{|\langle 1s|\,1s'\rangle}{N_{1s}N_{2px}} \frac{1}{i} Q\, b\, \mathrm{e}^{-QR} \left\{ -\frac{16}{b^6} + \frac{1}{a^3} \left[\frac{2}{c^3} + \frac{3+2aR}{a\,c^2} + \right.\right.$$

$$\left.\left. \frac{3+3aR+a^2R^2}{a^2c} \right] \mathrm{e}^{-cR} \right\}$$

$$M_z = 2\pi \frac{\langle 1s\,|\,1s'\rangle}{N_{1s}\,N_{2pz}} b\, \mathrm{e}^{-QR} \left\{ -\frac{16\,Q}{b^6} + \frac{1}{a^3} \left[\frac{2a}{c^3} + \frac{1+2aR}{c^2} + \frac{R+aR^2}{c} \right] \mathrm{e}^{-cR} \right\}.$$

$$\langle 1s\,|\,1s'\rangle = \frac{1}{N_{1s}\,N_{1s'}} \frac{8\pi}{(\alpha_1+\alpha_1')^3} \left\{ 1 - \frac{1}{4} [2 + (\alpha_1+\alpha_1')\,R]\, \mathrm{e}^{-(\alpha_1+\alpha_1')R} \right\}.$$

Notation:

$$a = \sqrt{\left(\alpha_1 + \frac{\alpha_2}{2}\right)^2 + Q}$$

$$b = \alpha_1 + \frac{\alpha_2}{2}$$

$$b' = \alpha_1 + \alpha_1'$$

$$c = a - Q.$$

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PRIVLAČNI ELEKTRONSKI POTENCIJAL HELIJEVA ATOMA NA SREDNJIM UDALJENOSTIMA OD POVRŠINE METALA ULOGA ATOMSKIH MATRIČNIH ELEMENATA

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U ovom radu promatran je privlačni elektronski potencijal helijeva atoma u prisutnosti površine u jellium modelu. Pri tome je primjenjena nelokalizirana dinamička Coulombova interakcija koja opisuje elektronske (jednočestične i kolektivne) fluktuacije u metalu. Pokazano je da podroban oblik atomskih matričnih elemenata i viši multipolni doprinosi dovode do jake modifikacije van der Waalsova privlačenja čak i kada zanemarimo disperziju i prigušenje elektronskih pobuđenja u metalu.