SURFACE PLASMONS AND INTERACTION OF CHARGES WITH THEIR IMAGES IN A " METAL - ATOM" SYSTEM

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The relation between surface plasmons and image charges in a "metal - atom" system is investigated. It is shown, that the interaction of external charge with image of another charge should be treated as a pair interaction of these external charges added to their Coulomb interaction. The perturbation operator responsible for the shift of atomic levels near a metal surface is constructed.

As it is known, surface plasmons (SP) are quasi-particles, bosons which correspond to normal modes of charge fluctuations on a metal surface, and which are responsible, from the quantum mechanical point of view, for long-range interaction between metal and the rest of the world [1]. SP in many respects determine evolution of "metal - moving atom" system, thus participating in different emission phenomena, which accompany bombardment of metals by accelerated ions. One kind of SP manifestation which occur in indicated system, namely, the long-range interaction between metal and atom is considered below. This question is discussed in connection with that fact, that in works [2,3] which were carried out recently, the operator of perturbation which is used in many models of ion emission and emission of excited atoms for calculation of shifts of atomic levels near the metal surface, from our point of view, probably was corrected in a wrong way.

Let's consider interaction between metal and system $\{e_i\}$ of classic charges e_i, which are placed in points $\mathbf{R}_i = (X_i, Y_i, Z_i)$. It is known, that in approximation, which is given by electrostatics of conductors, this interaction can formally be considered as Coulomb interaction between $\{e_i\}$ and system $\{e_i^*\}$ of fictitious charges $e_i^* = -e_i$, which are placed in points $(X_i, Y_i, -Z_i)$ (we consider, that the beginning of a frame is on a surface of metal, and the axis OZ is directed along the normal to this surface) [4]. In given approximation the energy of this interaction (or taken with an inverse sign work on infinitely slow removal of system $\{e_i\}$ to infinity)

$$E_{int} = \sum_i V(\mathbf{R}_i) + \tfrac{1}{2}\sum_{\substack{i,j \\ i\neq j}} W(\mathbf{R}_i,\mathbf{R}_j), \qquad (1a)$$

where

$$V(\mathbf{R}_i) = -\frac{e_i^2}{4Z_i}, \qquad (1b)$$

$$W(\mathbf{R}_i,\mathbf{R}_j) = -\frac{e_i e_j}{\sqrt{|\mathbf{R}_i - \mathbf{R}_j|^2 + 4Z_i Z_j}}. \qquad (1c)$$

It is possible to define $V(\mathbf{R}_i)$ value as energy of interaction of charge e_i with its image e_i^*, and W $(\mathbf{R}_i, \mathbf{R}_j)$ – as the sum of energies of interactions e_i with e_j^* and e_j with e_i^* [2-4]. The indicated approximation becomes valid when Z_i becomes large enough i.e. when there is no effect of macroscopic character of boundary conditions of an electrostatics of conductors.

A question arises: how it is possible to construct on the basis (1) the perturbation operator which is responsible for shifts of energy levels of atom, which is placed near (but not too close) the metal surface? This question was considered in details in works [2,3], where authors started from the assumption, that

$$E_{int} = \sum_i U_i, \qquad (2a)$$

Where U_i - potential energy of interaction of a charge e_i with metal. Taking into account (1a), naturally to put

$$U_i = V(\mathbf{R}_i) + \tfrac{1}{2}\sum_{\substack{j \\ i\neq j}} W(\mathbf{R}_i,\mathbf{R}_j). \qquad (2b)$$

From here for system $\{e_i\}$, which is classic analog of an one-electron atom, we have [2,3]:

$$U_e = V(\mathbf{R}_e) + \tfrac{1}{2}W(\mathbf{R}_e,\mathbf{R}_n), \qquad (3a)$$

$$U_n = V(\mathbf{R}_n) + \tfrac{1}{2}W(\mathbf{R}_e,\mathbf{R}_n), \qquad (3b)$$

where $\mathbf{R}_e$ and $\mathbf{R}_n$ - radius-vectors of an electron and core, correspondingly, and U_e and U_n - potential energies of these particles, conditioned by presence of metal. Considering a core to be a classical particle, authors of works [2,3] on the base of expression (3a) have constructed the perturbation operator which is responsible for shifts of energy levels of an one-electron atom near the metal surface, and have calculated these shifts. It is underlined in works [2,3], that earlier in similar calculations the energy

$$U_e = V(\mathbf{R}_e) + W(\mathbf{R}_e,\mathbf{R}_n). \qquad (4)$$

was wrongly assigned to an atomic electron.

Let's consider the question of expression (4) correctness. As it is clear from the stated above, it is not correct, if the assumption (2a) is valid. But it is possible to make the alternate assumption. In fact, the expressions (1a-c), which were found in approximation of the electrostatics of conductors, are consent to assumption, that only $V(\mathbf{R}_i)$ is a potential energy of interaction of a charge e_i with metal, and $W(\mathbf{R}_i, \mathbf{R}_j)$ is energy of pair interaction between e_i and e_j, which at the presence of metal is added to energy of a Coulomb interaction of charges. Such treatment of $W(\mathbf{R}_i, \mathbf{R}_j)$ value authorizes the use of expression (4) for calculation of atomic shifts and makes senseless the expression (3a). To be convinced of correctness of the proposed treatment, it is enough to show, considering the metal as system of SP, that, for example, in case of interaction of electrons with metal the following operator corresponds to $W(\mathbf{R}_i, \mathbf{R}_j)$ value

$$\hat{W} = \tfrac{1}{2}\int d^3\mathbf{r} \int d^3\mathbf{r}'\ \hat{C}^+(\mathbf{r})\hat{C}^+(\mathbf{r}')W(\mathbf{r},\mathbf{r}')\hat{C}(\mathbf{r}')\hat{C}(\mathbf{r}), \quad (5)$$

(here $C^+(\mathbf{r})$ and $C(\mathbf{r})$ - operators of birth and annihilation of an electron in a point $\mathbf{r}$) i.e. the operator of two-particle interaction [5]. Let's show it.

Let's write down a Hamiltonian of SP which not interact with the rest of the world. Using known "jellium" model for metal and neglecting a plasmons dispersion, we have [6,7]:

$$\hat{H}_{sp} = \sum_{\mathbf{q}}{}' \varepsilon\, \hat{a}_{\mathbf{q}}^+\hat{a}_{\mathbf{q}}, \qquad (6)$$

where $a_{\mathbf{q}}^+$, $a_{\mathbf{q}}$ - operators of creation and the annihilation of a surface plasmon with a wave vector $\mathbf{q}$ (all $\mathbf{q}$ are parallel to metal surface); ε - energy of a plasmon; slash near the sum means that vectors $\mathbf{q}$ fill the region of limited radius ($\mathbf{q} < q_c$). The second time quantized potential of an electric field generated by these plasmons is [6,7]

$$\hat{\Phi}(\mathbf{r}) = \sum_{\mathbf{q}}{}' \Gamma_q\,[\gamma(\mathbf{q},\mathbf{r})\hat{a}_q^+ + \gamma^*(\mathbf{q},\mathbf{r})\hat{a}_q], \qquad (7a)$$

where

$$\gamma(\mathbf{q},\mathbf{r}) = \exp(-q|z|-i\mathbf{q}\boldsymbol{\rho}), \qquad (7b)$$

$$\Gamma_q = (\pi\varepsilon/qS)^{1/2}. \qquad (7c)$$

Here $\boldsymbol{\rho}$ - parallel to the surface of metal component of a radius-vector $\mathbf{r}$; z - projection of $\mathbf{r}$ on the surface normal, S - surface area.

Let's consider two systems: "SP – electrons" (SP-el system) and "SP - electrons, as classical charges" (SP-$\{e_i\}$ system). Hamiltonian of interaction between SP and electrons for SP-el system

$$\hat{H}_{sp\text{-}el} = \int d^3\mathbf{r}\ \hat{n}(\mathbf{r})\hat{\Phi}(\mathbf{r}), \qquad (8)$$

where $\hat{n}(\mathbf{r}) = -e\hat{C}^{+}(\mathbf{r})\hat{C}(\mathbf{r})$ is the operator of electron charge density in the point **r**. The analogous operator for the SP-$\{e_i\}$ system

$$\hat{H}_{sp-\{e_i\}} = \sum_i e_i \hat{\Phi}(\mathbf{R}_i) \qquad (8')$$

(we use the former signs for values and radius-vectors of classic charges). On the base of (6)-(8) and (8'), introducing the convenient signs which are presented in the table

Table

SP-el system	**SP-$\{e_i\}$ system**
$\hat{X}_{\mathbf{q}} \equiv \varepsilon^{-1}\Gamma_q \int d^3\mathbf{r}\ \hat{n}(\mathbf{r})\gamma(\mathbf{q},\mathbf{r})$, $\hat{B}_{\mathbf{q}} \equiv \hat{a}_q + \hat{X}_{\mathbf{q}}$, $\hat{h}_{sp-el} \equiv -\sum_{\mathbf{q}}' \varepsilon \hat{X}_{\mathbf{q}}^{+} \hat{X}_{\mathbf{q}}$	$\chi_q \equiv \varepsilon^{-1}\Gamma_q \sum_i e_i\ \gamma(\mathbf{q},\mathbf{R}_i)$, $\hat{b}_{\mathbf{q}} \equiv \hat{a}_q + \chi_q$, $h_{sp-\{e_i\}} \equiv -\sum_{\mathbf{q}}' \varepsilon\chi_q{}^{*}\chi_q$

we can write

$$\hat{H}_{sp} + \hat{H}_{sp-el} = \sum_{\mathbf{q}}' \varepsilon \hat{B}_{\mathbf{q}}^{+} \hat{B}_{\mathbf{q}} + \hat{h}_{sp-el} \qquad (9)$$

$$\hat{H}_{sp} + \hat{H}_{sp-\{e_i\}} = \sum_{\mathbf{q}}' \varepsilon \hat{b}_{\mathbf{q}}^{+} \hat{b}_{\mathbf{q}} + h_{sp-\{e_i\}} \qquad (9')$$

It is easy to become convinced, that at any **q**, **q**' the operators $\hat{X}_{\mathbf{q}}$, $\hat{X}_{\mathbf{q}}^{+}$ commute with $\hat{X}_{\mathbf{q}'}$. Correspondingly, the operators $\hat{B}_{\mathbf{q}}^{+}$, $\hat{B}_{\mathbf{q}'}$ obey to the same commutation relations, as $\hat{a}_q{}^{+}$, $\hat{a}_{q'}$ operators, i.e. to the standard commutation relations [5] for the operators of creation and annihilation of bosons. The latter is valid also in relation to the $\hat{b}_{\mathbf{q}}^{+}$, $\hat{b}_{\mathbf{q}'}$ operators because χ_q values are not the operators, but usual complex figures. It is clear also, that $h_{sp-\{e_i\}}$ is a material value with dimensionality of energy.

Let's clarify physical sense of addends in the right part of expressions (9), (9'). For this let's find at first $h_{sp-\{e_i\}}$. Doing replacement [6,7]

$$\sum_{\mathbf{q}}' \ldots \rightarrow S/(2\pi)^2 \int_{|q|<q_c} d^2\mathbf{q} \ldots, \qquad (10)$$

we find (see Appendix A)

$$h_{sp-\{e_i\}} = \sum_i \hat{V}(\mathbf{R}_i) + \tfrac{1}{2}\sum_{\substack{i,j \\ i\neq j}} \hat{W}(\mathbf{R}_i,\mathbf{R}_j), \qquad (11a)$$

where

$$\hat{V}(\mathbf{R}_i) = -\frac{e_i^2}{4|Z_i|}[1-\exp(-2q_c|Z_i|)], \qquad (11b)$$

$$\hat{W}(\mathbf{R}_i,\mathbf{R}_j) = -e_ie_j \int_0^{q_c} dq\ \exp[-q(|Z_i|+|Z_j|)]\ J_0(q|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j|). \qquad (11c)$$

Here $\boldsymbol{\rho}_i$ and $\boldsymbol{\rho}_j$ – parallel to the metal surface components of $\mathbf{R}_i$ and $\mathbf{R}_j$ vectors, $J_0(x)$ - Bessel function of I kind of 0 order. At large enough Z_i ($Z_i >> q_c{}^{-1}$) the value $h_{sp-\{e_i\}}$ coincides with energy of interaction E_{int}, becouse in this area expressions (11b-c) are transformed to expressions (1b-c). Regarding this result and mentioned above commutation relations for the operators $\hat{b}_{\mathbf{q}}^{+}$,

$\hat{b}_{q'}$, it is possible to come to the conclusion, that $\sum_q' \varepsilon\ \hat{b}_q^+ \hat{b}_q$ is a Hamiltonian of system of new quasi-particles - surface plasmons, whose properties are changed by the presence of classical charges e_i. This modified surface plasmons (mSP) have the same energies, as SP, but differ from last by ground and exited states. In particular, the ground state |G > of the system mSP is determined by the equation

$$\hat{b}_q|G\rangle = 0, \quad \text{or} \quad \hat{a}_q|G\rangle = -\chi_q|G\rangle,$$

where **q** transverses all possible values. When all $Z_i \to \infty$, then $\chi_q \to 0$, i.e. $a_q|G\rangle = 0$ at all **q** and |G > state transfers in a ground state of the SP system. At infinitely slow removal of charges e_i to infinity, the mSP system , if initially it was in a state |G >, will still stay in this state (this state is in parametric dependence from Z_i), i.e. the energy of the plasmon system will not change. Therefore the $h_{sp\text{-}\{e_i\}}$ value as well as E_{int}, is equal to the work (with an inverse sign) on infinitely slow removal of system $\{e_i\}$ to infinity, i.e. quantities $h_{sp\text{-}\{e_i\}}$ and E_{int} have the same physical sense. Now physical sense of addends in a right part of expression (9) becomes evident: $\sum_q' \varepsilon\ \hat{B}_q^+ \hat{B}_q$ is a Hamiltonian of system of surface plasmons, the properties of which are changed by presence of electrons over the metal surface, and operator $\hat{h}_{sp-el}$, classical analog of which is $h_{sp\text{-}\{e_i\}}$ value, is operator which is responsible for shifts of energy levels of electrons near the of metal surface. The last task is to obtain physically transparent equation for $\hat{h}_{sp-el}$.

Using the known commutation relations for the fermion operators $\hat{C}^+(\mathbf{r})$, $\hat{C}(\mathbf{r})$ and the results of calculating of $h_{sp\text{-}\{e_i\}}$ value, we find (see Appendix A)

$$\hat{h}_{sp-el} = \int d^3\mathbf{r}\ \hat{C}^+(\mathbf{r})\tilde{V}(\mathbf{r})\hat{C}(\mathbf{r}) + +\tfrac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\hat{C}^+(\mathbf{r})\hat{C}^+(\mathbf{r}')\tilde{W}(\mathbf{r},\mathbf{r}')\hat{C}(\mathbf{r}')\hat{C}(\mathbf{r}). \quad (12)$$

The classical analogs of the first and the second operator additives in (12), when the electrons are placed, mainly, on large distances from a metal surface ($\gg q_c^{-1}$), are values $V(\mathbf{R}_i)$ and $W(\mathbf{R}_i,\mathbf{R}_j)$ correspondingly. Thus, the operator of a two-particle interaction (5) really corresponds to the $W(\mathbf{R}_i,\mathbf{R}_j)$ energy. It proves validity of the assumption, made by us, that $W(\mathbf{R}_i, \mathbf{R}_j)$ is energy of the pair interaction of charges, which is caused by presence of metal.

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ПОВЕРХНЕВІ ПЛАЗМОНИ ТА ВЗАЄМОДІЯ ЗАРЯДІВ ІЗ ЇХ ЕЛЕКТРИЧНИМИ ЗОБРАЖЕННЯМИ В СИСТЕМІ “МЕТАЛ-АТОМ”.

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Досліджено взаємозв’язок поверхневих плазмонів з електричними зображеннями зарядів в системі “металл - атом”. Показано, що взаємодія заряду з електричним зображенням іншого заряду є парною. Одержано вираз для енергії цієї взаємодії, який, на відміну від відомого, не містить розбіжностей. За його допомогою побудовано оператор збурення, що відповідає за зсуви енергетичних рівнів атому поблизу поверхні металу.

Appendix A

CALCULATION OF $h_{sp\text{-}\{e_i\}}$ AND $\hat{h}_{sp-el}$ VALUES

Coming out from the definition of $h_{sp\text{-}\{e_i\}}$ we can write

$$h_{sp\text{-}\{e_i\}} = \sum_i \tilde{V}(\mathbf{R}_i) + ½ \sum_{\substack{i,j \\ i\neq j}} \tilde{W}(\mathbf{R}_i,\mathbf{R}_j), \tag{A1}$$

where

$$\tilde{V}(\mathbf{R}_i) = - e_i^2 \sum_{\mathbf{q}}{}' \varepsilon^{-1}\Gamma_q^2 |\gamma(\mathbf{q},\mathbf{R}_i)|^2, \tag{A2}$$

$$\tilde{W}(\mathbf{R}_i,\mathbf{R}_j) = - 2e_ie_j \sum_{\mathbf{q}}{}' \varepsilon^{-1}\Gamma_q^2 \gamma^*(\mathbf{q},\mathbf{R}_i)\, \gamma(\mathbf{q},\mathbf{R}_j). \tag{A3}$$

Sums in (A2) and (A3) after replacing them with integrals (10) appear in a following manner:

$$\sum_{\mathbf{q}}{}' \varepsilon^{-1}\Gamma_q^2 \ldots = \frac{1}{4\eth}\int_0^{q_c} dq \int_0^{2\eth} d\varphi \ldots, \tag{A4}$$

Where q, φ – polar coordinates of vector **q**. This substitution results in:

$$\tilde{V}(\mathbf{R}_i) = -\frac{e_i^2}{2}\int_0^{q_c} dq\ \exp(-2q|Z_i|), \tag{A5}$$

$$\tilde{W}(\mathbf{R}_i,\mathbf{R}_j) = -\frac{e_ie_j}{2\pi}\int_0^{q_c} dq\ \exp[-q(|Z_i|+|Z_j|)]\int_0^{2\eth} d\varphi\ \exp(iq|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j|), \tag{A6}$$

where $\boldsymbol{\rho}_i$ и $\boldsymbol{\rho}_j$ – parallel to the metal surface components of $\mathbf{R}_i$ and $\mathbf{R}_j$ vectors.

Calculating the integral in (A5) we get:

$$\tilde{V}(\mathbf{R}_i) = -\frac{e_i^2}{4|Z_i|}[1-\exp(-2q_c|Z_i|)]. \qquad (A7)$$

Let's notice that in region of large positive Z_i ($Z_i >> q_c^{-1}$), where (1a-c) equations are valid, the expression (A7) transforms into expression (1b) for the potential energy $V(\mathbf{R}_i)$.

Let's simplify the (A6) equation. We have [8]:

$$\int_0^{\pi} \exp(i\, x \cos\varphi)\, d\varphi = \pi J_0(x),$$

where $J_0(x)$ – Bessel function of I kind of 0 order. Thus:

$$\tilde{W}(\mathbf{R}_i,\mathbf{R}_j) = -e_i e_j \int_0^{q_c} dq\ \exp[-q(|Z_i|+|Z_j|)]\, J_0(q|\boldsymbol{\rho}_i-\boldsymbol{\rho}_j|). \qquad (A8)$$

The integral in (A8) is calculated analytically, when $|Z_i|+|Z_j| >> q_c^{-1}$. In this case we have [8]:

$$\tilde{W}(\mathbf{R}_i,\mathbf{R}_j) \underset{|Z_i|+|Z_i|>>q_c^{-1}}{=} -\frac{e_i e_j}{\sqrt{|\mathbf{R}_i-\mathbf{R}_j|^2+|2Z_iZ_j|+2Z_iZ_j}}. \qquad (A9)$$

Let's notice that in region of large positive Z_i, Z_j, where (1a-c) equations are valid, the expression (A9) transforms into expression (1c) for the energy $W(\mathbf{R}_i,\mathbf{R}_j)$. It is interesting also to note, that when the charges e_i and e_j are located in the opposite sides from the metal surface, their interaction with each other through electric images compensate fully, according to (A9), their Coulomb interaction.

Let's find out now the $\hat{h}_{sp-el}$ operator. Coming out from its definition we can write:

$$\hat{h}_{sp-el} = \int d^3\mathbf{r} \int d^3\mathbf{r}'\ \hat{C}^+(\mathbf{r})\hat{C}(\mathbf{r})\{-e^2{\sum_{\mathbf{q}}}' \varepsilon^{-1}\Gamma_q^2\gamma^*(\mathbf{q},\mathbf{r})\,\gamma(\mathbf{q},\mathbf{r}')\}\hat{C}^+(\mathbf{r}')\hat{C}(\mathbf{r}'). \qquad (A10)$$

Commuting first the $\hat{C}(\mathbf{r})$, $\hat{C}^+(\mathbf{r}')$ operators and then $\hat{C}(\mathbf{r})$, $\hat{C}(\mathbf{r}')$ operators in (A10) and taking the integral on $\mathbf{r}'$ in the additive, which arise during these operations and which contains delta function $\delta^3(\mathbf{r}-\mathbf{r}')$, finally we get, taking into account (A2), (A3):

$$\hat{h}_{sp-el} = \int d^3\mathbf{r}\,\hat{C}^+(\mathbf{r})\,\tilde{V}(\mathbf{r})\hat{C}(\mathbf{r}) + \tfrac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\,\hat{C}^+(\mathbf{r})\hat{C}^+(\mathbf{r}')\,\tilde{W}(\mathbf{r},\mathbf{r}')\hat{C}(\mathbf{r}')\hat{C}(\mathbf{r}). \qquad (A11)$$