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CALCULATIONS OF FIELD DESORPTION AND FIELD IONIZATION

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The single-cesium-atom adsorption and field ionization process of H and He atoms in the presence of external positive electric field is considered. The energy shift, the width of the broaden atomic energy level and effective charge on adatom are self-consistently calculated as a function of external electric field. The influence of an external electric field on the shift and broadening of energy level of hydrogen and helium atoms and the indirect influence of these characteristics on critical distance of field ionization is also considered.

1. Introduction

In many cases adsorption is investigated experimentally in the presence of an external electric field of the strength, *F*, [1]. On the other hand, the electric field plays a great role in the field ion microscope, where positive ions of the image gas are produced [2]. The theory of adsorption in the presence of an external electric field was given by Bennett and Falicov [3], and some theoretical considerations connected with this problem were given recently [1]. The theory of field ionization in the field ion microscopy regime was discussed previously [4]. However, the papers quoted above neglected the spatial contribution to the shift of energy levels of atomic electrons and do not discuss the dependence of the desorption energy or field ionization process on the energy shift and broadening of the atomic electron.

In this paper we shall consider both the desorption and field ionization processes. In the first case we shall consider single-cesium-atom adsorption. In the case of field ionization process we shall consider the influence of an external electric field on the shift and broadening of the energy level of hydrogen and helium atoms and the indirect influence of these characteristics on the critical distance of field ionization.

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2. *Description of the system*

In order to calculate the Hamiltonian of a bond electron of adatom we use, for simplicity, the classical image energy potential. This energy may be written in the form

$$V(\xi) = \frac{e}{4\pi\varepsilon_0}\left[qD^{-1} - e(4d+\lambda)^{-1}\right], \qquad \lambda = 0, \tag{1}$$

where ε_0 is the dielectric constant of the vacuum, and q denotes the effective charge of adatom (adion) $q = Z_{\text{eff}}|e|$ (e is the electron charge). The distances, D and d, are defined in Fig. 1a, and λ is a quantity which appears in the potential where quantum corrections to the image potential are included.

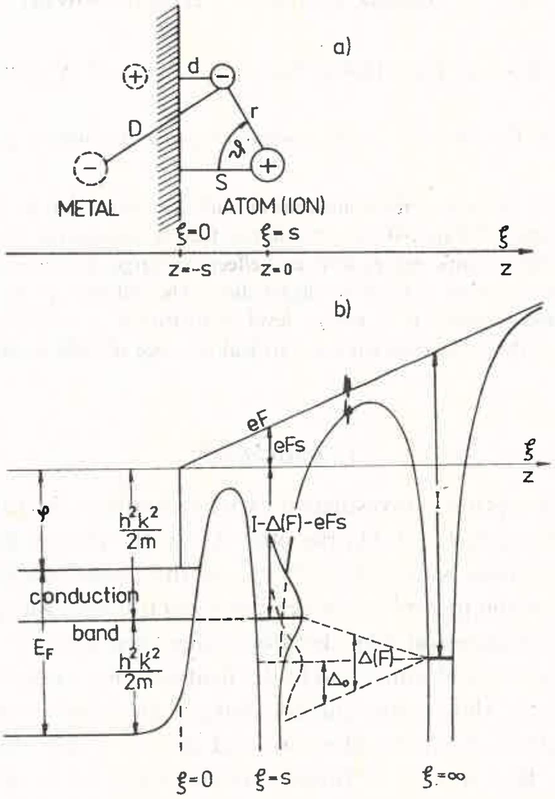

Fig. 1. Spatial (a) and energetic (b) representation of the adatom (adion) near the metal surface in the external electric field F

The Hamiltonian of the bound electron in the presence of an external electric field F, can be written in the form [5]

$$H_{\text{ef}} = H_{\text{a}} + H'_{\text{a-m}}, \tag{2}$$

where

$$H_{\text{a}} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{eq}{4\pi\varepsilon_0 r} \tag{2a}$$

is the Hamiltonian of an atomic electron, and

$$H'_{\text{a-m}} = \frac{e}{4\pi\varepsilon_0}\left(\frac{q}{D} - \frac{e}{4d}\right) + eFd \tag{2b}$$

represents the perturbation caused by the metallic surface and external electric field. On the other hand, a quasi-free electron in metal is perturbed by the presence of the ion core and the external electric field

$$H_{\text{ef}} = H_{\text{m}} + H'_{\text{m-a}}, \tag{3}$$

where

$$H_{\text{m}} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e}{4\pi\varepsilon_0}\left(\frac{q}{D} - \frac{e}{4d}\right), \tag{3a}$$

$$H'_{\text{m-a}} = -\frac{eq}{4\pi\varepsilon_0 r} + eFd, \quad d \geqslant s_0. \tag{3b}$$

The distance, s_0, corresponds to the distance at which the potential, $V(\xi)$, is equal to the constant potential, V_0, of the electrons within the metal. Thus s_0 is the root of the equation

$$V_0(s_0) = E_{\text{F}} + \varphi, \tag{4}$$

where $V(\xi)$ is defined by (1), E_{F} is the Fermi energy and φ is the work function of metal.

The atomic electron is described by exact the wave function $\psi_{\text{A}} = |A\rangle$ for the hydrogen atom

$$\psi_{\text{A}}^{\text{H}} = \pi^{-1/2} a_0^{-3/2} e^{-\frac{r}{a_0}}, \tag{5}$$

where a_0 is the Bohr radius, and by the following function for cesium atom [5]

$$\psi_{\text{A}}^{\text{Cs}} = \frac{a^{3/2}}{\sqrt{\pi}}(1-ar)e^{-ar}, \quad a = 0.99\ \text{Å}^{-1}. \tag{6}$$

The solution of Schrödinger's equation with the Hamiltonian, H_{m}, can be written as [5]

$$\psi_{\text{e}} = C \exp\left[i(k_1 x + k_2 y)\right] \exp(ik_3\xi). \tag{7}$$

In (7), the constant, C, is calculated from the condition $\psi_{\text{e}}(\xi = 0) = \psi_{\text{M}}$, where the eigenfunction of an electron in metal is given by [5]

$$\psi_{\text{M}} = (1/k_v L^{3/2}) \exp\left[i(k_1 x + k_2 y)\right]\left[(k'_3 + k_3)\exp(ik'_3\xi) + (k'_3 - k_3)\exp(-ik'_3)\right]. \tag{8}$$

L is the length of a sufficiently large cubic metal; k and k' are wavenumbers of the electron according to the origin of the energy scale (Fig. 1b). The indices 1–3 indicate the projections on the directions of Ox, Oy and Oz; k and k_3 are positive imaginary numbers; and k_v is defined by

$$\frac{\hbar^2 k_v^2}{2m} = E_F + \varphi. \tag{9}$$

Finally,

$$\psi_M = (k_v L^{3/2})^{-1} \exp[i(k_1 x + k_2 y)] 2k_3' \exp(ik_3 \xi). \tag{10}$$

3. Energy level shift

It is well known [5, 6], that when an atom interacts with a metal surface the perturbation, H'_{a-m}, caused by the metallic surface, shifts the atomic level with respect to the Fermi level of metal. The first order shift in the absence of an external electric field is given by

$$\Delta E_0 \equiv \Delta_0 = \frac{\left\langle A \left| \frac{e}{4\pi\varepsilon_0}\left(\frac{q}{D} - \frac{e}{4d}\right) \right| A \right\rangle}{\langle A|A\rangle}. \tag{11}$$

In the presence of a positive external field, F, the energy shift is equal to

$$\Delta E(F) \equiv \Delta(F) = \frac{\langle A|H'_{a\text{-}m}|A\rangle}{\langle A|A\rangle} = \Delta_0 + eF\frac{\langle A|d|A\rangle}{\langle A|A\rangle}. \tag{12}$$

Because the distance of an electron from the metal surface is given by $d = s + r\cos\vartheta = s + z$, and the distance between the electron and the ion core image is given by $D \sim 2s + r\cos\vartheta = 2s + z$ (a good approximation for r is small compared to s), we may write

$$\Delta(F) = \frac{e^2}{4\pi\varepsilon_0} \frac{\left\langle A \left| \frac{q}{2s+z} - \frac{e}{4(s+z)} \right| A \right\rangle}{\langle A|A\rangle} + eFs + eF\frac{\langle A|z|A\rangle}{\langle A|A\rangle}. \tag{13}$$

In (13), the integration has been restricted to the region outside the metal. The integrals of a type

$$\frac{1}{2\pi}\int_{-(s-s_0)}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} r^n e^{-\alpha r}\,dx\,dy\,dz \equiv K_n(\alpha),$$

and

$$\frac{1}{2\pi}\int_{-(s-s_0)}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} r^n e^{-\alpha r}\frac{dx\,dy\,dz}{z+m} \equiv I_n(m, \alpha),$$

where $n = -1, 0, 1, 2, 3, \ldots, R \ni \alpha$, $m > 0$, $s - s_0 > 0$, are computed in [7], and are given in Appendix I. Finally, the first order energy level shift is expressed by

$$\Delta(F) = \frac{e^2}{4\pi\varepsilon_0} \frac{Z_{\text{eff}} I_0(2s, 2a) - I_0(s, 2a)/4}{K_0(2a)} + eFs + eFZ_0(2a)/K_0(2a), \quad \text{for H}, \tag{14}$$

and by

$$\Delta(F) = \frac{e^2}{4\pi\varepsilon_0} \frac{Z_{\text{eff}} I_0(2s, 2a) - I_0(s, 2a)/4 - 2Z_{\text{eff}} I_1(2s, 2a)}{K_0(2a) - 2aK_1(2a) + a^2 K_2(2a)}$$

$$+ \frac{aI_1(s, 2a)/2 + Z_{\text{eff}} a^2 I_2(2s, 2a) + eF[Z_0(2a) - 2aZ_1(2a) + a^2 Z_2(2a)]}{K_0(2a) - 2aK_1(2a) + a^2 K_2(2a)} + eFs, \quad \text{for Cs}. \tag{15}$$

The functions $Z_n(\alpha)$ are given in Appendix II, and the energy shifts Δ_0 and $\Delta(F)$ are shown schematically in Fig. 1b. Using this figure we may determine the wavenumber, k', which is equivalent to the electron energy, with zero energy at the bottom of the conduction band. Because k' is determined by the position of the shifted atomic level it is a function of s

$$\frac{\hbar^2 k'^2(s)}{2m} = \varphi + E_{\text{F}} - [I - \Delta(F) - eFs], \tag{16}$$

where I is the ionization energy of atom.

4. *Level broadening* (*the probability per unit time of the transition of the electron from the atomic level to the metal*)

As was pointed out by Gurney [6], when the atom is brought closer to the metal the interaction of the atom with metal also causes the broadening of the atomic (ionic) level. The quantity, Γ, determining the width of the broaden energy level is related to the transition probability per unit time of transition of the electron from the atomic level to metal

$$\Gamma \simeq \frac{mkL^3}{\hbar^2 2\pi^2} \int_0^{2\pi} d\varphi \int_0^{\pi/2} |V_{\text{i}\to\text{f}}|^2 \sin \vartheta d\vartheta \equiv \hbar W, \tag{17}$$

where k is the wavenumber of the electron according to the origin of the level (Fig. 1b), and

$$V_{\text{i}\to\text{f}} \sim \langle M | H'_{\text{m-a}} | A \rangle. \tag{18}$$

Substituting (3) into (18) and performing integrations (Appendix III) we have

$$\Gamma \equiv \Gamma(F, s, Z_{\text{eff}})$$

$$= \frac{4a^4}{V_0} \int_{a^2}^{a^2+(k')^2} \frac{\sqrt{(k')^2 + a^2 - x}}{k'} e^{-2s\sqrt{x}} \left[-14.4 Z_{\text{eff}} \frac{s}{\sqrt{x}} + \left(\frac{as^3}{6x} + \frac{as^2}{2x^{3/2}} \right) F \right]^2 dx, \tag{19}$$

for the hydrogen atom, and

$$\Gamma \equiv \Gamma(F, s, Z_{\text{eff}})$$

$$= \frac{4a^4}{V_0} \int_{a^2}^{a^2+(k')^2} \frac{\sqrt{(k')^2+a^2-x}}{k'} e^{-2s\sqrt{x}} \left[-14.4Z_{\text{eff}} \left(-\frac{a^2s^2}{2x} + \frac{x-a^2}{x^{3/2}} \right) \right.$$

$$\left. + \left[-\tfrac{1}{12} \frac{a^3}{x^{3/2}} s^4 + \tfrac{1}{6} \left(\frac{2a}{x} - \frac{3a^3}{x^2} \right) s^3 + \tfrac{1}{2} \left(\frac{2a}{x^{3/2}} - \frac{3a^3}{x^{5/2}} \right) s^2 \right] F \right\}^2 dx, \tag{20}$$

for the cesium atom.

5. *Self-consistent calculation of the effective charge on adatom (adion)*

As can be seen from the above considerations, both the energy shift, ΔE, and width, Γ, depend on the effective charge number, Z_{eff}

$$\Delta E = \Delta E(s, F, Z_{\text{eff}}), \qquad \Gamma = \Gamma(s, F, Z_{\text{eff}}). \tag{21}$$

On the other hand, Z_{eff} is a function of Δ and Γ [3, 8]

$$Z_{\text{eff}} = 1 - \frac{1}{\pi} \left\{ \operatorname{arctg} \left[\frac{I - \Delta(s, F, Z_{\text{eff}}) - \varphi_{hkl}}{\Gamma(s, F, Z_{\text{eff}})} \right] + \frac{\pi}{2} \right\}. \tag{22}$$

Thus, for calculating Z_{eff} equations (21–22) must be solved self-consistently. Note that the effective charge depends also on the crystallographic direction of the considered plane of a metallic monocrystal. This dependence enters in (22) via $\varphi = \varphi(hkl)$, where h, k, l are Müller indices.

6. *Results and discussion*

Below we shall give the results of numerical calculations. All these calculations were carried out for hydrogen, helium and cesium atoms close to the tungsten surface. For tungsten, we have accepted $n = 6$ conducting electrons per atom. This number is the chemical valency of *W*. Such a number of free electrons per atom gives a Fermi energy equal

TABLE I

Parameters of H and Cs atoms and of the metal used in numerical computations

Atom	a(Å^{-1})	I(eV)	Metal
H	1.89	13.54	$\varphi = 4.5$ eV
Cs	0.99	3.86	$E_F = 18.99$ eV

to 18.99 eV. It should be noted that the earlier works were based on the assumption that the Fermi energy of tungsten is approximately 10 eV. However, as follows from numerical calculations, the final results are practically identical for both values of the Fermi energies.

All parameters used in numerical computations are given in Table I.

(*i*) *Adsorption of cesium.* The computed self-consistent values of the effective charge, Z_{eff}, on adatom, the energy shift, Δ, and the width of the broaden energy level, Γ, as a function of the external field strength, F, are given for cesium in Table II for $s = 3$ Å. From the data in Table II it follows that the external field weakly influences the effective charge of cesium adion and the width, but distinctly changes the energy shift, Δ.

TABLE II

Field (F) dependences of: effective charge $Z = Z_{\text{eff}}$ on adatom, energy shift, Δ, and the width, Γ, for $s = 3$ Å

F(V/Å)	Z	Δ (eV)	Γ (eV)
0.1	0.891	0.810	0.512
0.2	0.910	1.189	0.516
0.3	0.925	1.553	0.512
0.4	0.936	1.907	0.504
1	0.970	3.951	0.420

Taking the value of the desorption field as $F_{\text{D}} = 0.3$ and 0.4 V/Å (according to [1]) and values of $\Delta(F)$ and Γ from Table II, we observe that the quantity

$$\frac{\varepsilon_{\text{F}}}{\frac{1}{2}\Gamma} \equiv \frac{\varphi - I + \Delta(F)}{\frac{1}{2}\Gamma}$$

is much greater than unity. This confirms the suggestion of Todd and Rhodin [1], that only the extreme tail of the Lorentzian state will overlap the occupied metal states upon application of F_{D}.

Approximating the dependence of the effective charge of F given in Table II by the expression

$$Z_{\text{eff}}(F) = 0.11F + 0.88,$$

one may estimate the change in the adsorption energy as a function of the external field, as follows:

$$\Delta q(F) = e^2 Z^2_{\text{eff}}(F) \int\limits_{s=3\text{Å}}^{\infty} \frac{dz}{4(z+k_s^{-1})} - q_0 \sim 0.193F,$$

where k_s^{-1} is the screening length (= 0.6 Å for tungsten) and q_0 is the adsorption heat for $F = 0$.

This result is in accordance with experimental observations [9].

(*ii*) *Critical distance of field ionization.* It is well known [2] that there is a critical distance, s_c^0, below which the image atoms can not be ionized in the field ion microscope. This distance is determined by a condition where at s_c^0 the following equality is fulfilled:

$$\varphi + \frac{e^2}{4s_c^0} + eFs_c^0 = I + \tfrac{1}{2}F^2(\alpha_a - \alpha_i), \tag{23}$$

where α_a and α_i are the polarizabilities of an atom and of a created ion, respectively. Because the difference $e^2/4s_c^0 - \frac{1}{2}F^2(\alpha_a - \alpha_i)$ is small in comparison with $I - \varphi$ we may neglect it. This gives

$$\varphi + eFs_c^0 \sim I. \tag{23a}$$

However, expressions (23) and (23a) are not quite correct from the quantum-mechanical point of view. That is, as can be seen from (13), the energy shift in the presence of an external electric field is the sum of the zero-field energy shift, Δ_0, and the field depending terms. Therefore, condition (23a), determining the critical distance, s_c^0, changes to the form (Fig. 1b)

$$\varphi + eFs_c \sim I - \Delta(F). \tag{24}$$

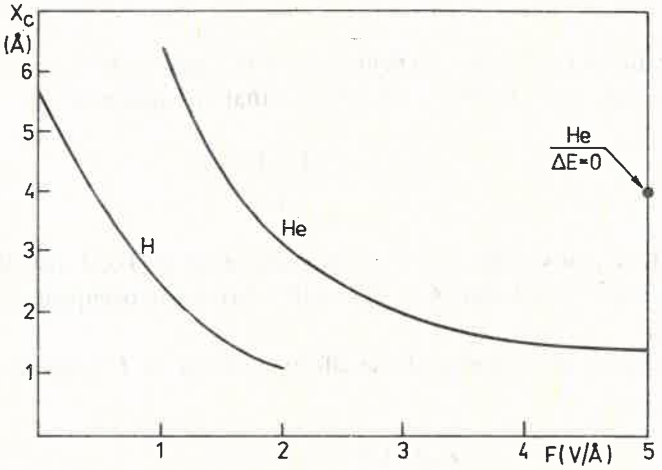

Fig. 2. The critical distance, s_c, of field ionization vs field strength F

The self-consistently computed dependence of s_c on F is shown in Fig. 2. The procedure for the computation of $s_c(F)$ for helium is described in [10]. From Fig. 2 it follows that the true value of the critical distance should be smaller than that computed from (23a) for proper values of ionizing field strengths.

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APPENDIX I

$$K_n(\alpha) = \alpha^{-n-3}\{2(n+2)!-e^{-\alpha(s-s_0)}S\},$$

$$S = \sum_{k=0}^{n+1} \frac{(n+2-k)\,(n+1)!}{k!}\, a^k(s-s_0)^k,$$

$$I_n(m, a) = a^{-n-2}\left\{\sum_{l=0}^{n}\left[\binom{n+1}{l}\left[\sum_{k=0}^{n-l} \frac{(n-l)!}{(n-l-k)!}(ma)^{n-l-k}\right]\right.\right.$$

$$\times\left[\sum_{k=0}^{l}(-1)^{l-k}\frac{l!}{(l-k)!}(ma)^{l-k}\right]$$

$$+\sum_{l=0}^{n}\binom{n+1}{l}\left[\sum_{k=0}^{n-l}(-1)^{n-l-k+1}\frac{(n-l)!}{(n-l-k)!}(ma)^{n-l-k}\right]\left[\sum_{k=0}^{l}\frac{l!}{(l-k)!}(ma)^{l-k}\right]\Bigg]$$

$$+\left[\sum_{k=0}^{n+1}\frac{(n+1)!}{(n+1-k)!}(am)^{n+1-k}\right]e^{-am}\int_{af}^{am}\frac{e^t}{t}\,dt$$

$$+\left[\sum_{k=0}^{n+1}(-1)^{n+1-k}(am)^{n+1-k}\frac{(n+1)!}{(n+1-k)!}\right]e^{am}\int_{am}^{\infty}\frac{e^{-t}}{t}\,dt$$

$$+e^{-a(s-s_0)}\left[\sum_{l=0}^{n}\binom{n+1}{l}\sum_{k=0}^{n-l}(-1)^{n-l-k}\frac{(n-l)!}{(n-l-k)!}(fa)^{n-l-k}\right]$$

$$\times\left[\sum_{k=0}^{l}\frac{l!}{(l-k)!}(ma)^{l-k}\right]\Bigg\},$$

$$f = -(s-s_0)+m.$$

APPENDIX II

$$Z_{-1}(\alpha) = \frac{1}{2\pi} \int\limits_{-(s-s_0)}^{\infty} \iint\limits_{-\infty}^{\infty} dzdxdy \frac{z}{r} e^{-\alpha r}.$$

Using the inverse of the Fourier transform [5]

$$\frac{e^{-ar}}{r} = \frac{1}{2\pi^2} \iiint\limits_{-\infty}^{\infty} d^3\chi \frac{e^{i\chi \cdot r}}{a^2+\chi^2}$$

we have:

$$Z_{-1}(\alpha) = \frac{1}{4\pi^3} \int\limits_{-(s-s_0)}^{\infty} dzz \int\limits_{-\infty}^{\infty} d^3\chi dxdy \frac{e^{i\chi \cdot r}}{\alpha^2+\chi^2}$$

$$= \frac{1}{\pi} \int\limits_{-(s-s_0)}^{\infty} dzz \iiint\limits_{-\infty}^{\infty} d^3\chi e^{i\chi_3 z} \frac{1}{\alpha^2+\chi^2} \delta(\chi_1)\delta(\chi_2) = e^{-(s-s_0)\alpha} \left[\frac{s-s_0}{\alpha^2} + \frac{1}{\alpha^3}\right].$$

The χ_3 integration was done by calculating the residues at the poles $\chi_3 = i\alpha$ when $z \geqslant 0$, and $\chi_3 = -i\alpha$ when $z < 0$. The other integrals are obtained by differentiation with respect to the parameter, α:

$$Z_0(\alpha) = -\frac{\partial}{\partial\alpha} \int\limits_{-(s-s_0)}^{\infty} \iint\limits_{-\infty}^{\infty} dzdxdy \frac{z}{r} e^{-\alpha r} = (s-s_0)\left[\frac{s-s_0}{\alpha^2} + \frac{1}{\alpha^3}\right] e^{-(s-s_0)\alpha}$$

$$+ \left[\frac{s-s_0}{2^{-1}\alpha^3} + \frac{3}{\alpha^4}\right] e^{-(s-s_0)\alpha} = \left[\frac{(s-s_0)^2}{\alpha^2} + \frac{3(s-s_0)}{\alpha^3} + \frac{3}{\alpha^4}\right] e^{-(s-s_0)\alpha},$$

$$Z_1(\alpha) = -\frac{\partial}{\partial\alpha} Z_0(\alpha), \quad Z_2(\alpha) = -\frac{\partial}{\partial\alpha} Z_1(\alpha).$$

APPENDIX III

$$V_{\mathrm{i}\to\mathrm{f}} \simeq \langle \psi_A | H'_{pf} | \psi_M \rangle = C \int\limits_{-s}^{0} e^{ik_3\xi} \iint\limits_{-\infty}^{\infty} \frac{1}{r} \exp\left[-ar + i(k_1 x + k_2 y)\right] f dzdxdy$$

$$+ D \int\limits_{-s}^{0} e^{ik_3\xi}(s+z) \iint\limits_{-\infty}^{\infty} e^{i(k_1 x + k_2 y)} e^{-ar} f dzdxdy,$$

$$C = -\frac{Z_{\mathrm{eff}} e^2}{4\pi\varepsilon_0} \frac{N}{k_v L^{3/2}} 2k'_3, \quad D = eF \frac{N}{k_v L^{3/2}} 2k'_3,$$

where $f = 1$ for H and $f = 1 - ar$ for Cs, $N = a^{3/2}\pi^{-1/2}$.

The integral has been restricted to the region outside the metal [5, 6]. Now we shall compute the integral of the type

$$\iint_{-\infty}^{\infty} e^{\,i(k_1x+k_2y)} r^n e^{-ar} dxdy,$$

where $n = -1, 0, 1, 2, \ldots$ Using the inverse of the Fourier transform

$$\frac{e^{-ar}}{r} = \frac{1}{2\pi^2}\iiint_{-\infty}^{\infty} \frac{e^{i\chi\cdot r}}{a^2+\chi^2}\, d^3\chi, \qquad \chi^2 = \chi_1^2+\chi_2^2+\chi_3^2,$$

we have

$$\iint_{-\infty}^{\infty} e^{i(k_1x+k_2y)} r^{-1} e^{-ar} dxdy = 2\int_{-\infty}^{\infty} \frac{e^{i\chi_3 z}}{a^2+\chi^2}\,\delta(k_1+\chi_1)\delta(k_2+\chi_2)d^3\chi$$

$$= 2\int_{-\infty}^{\infty} \frac{e^{i\chi_3 z}}{a^2+k_1^2+k_2^2+\chi_3^2}\, d\chi_3 = 4\pi i\left[\frac{e^{i\chi_3 z}}{\chi_3+\varepsilon i G}\right]_{\chi_3=\varepsilon iG} = 2\pi\,\frac{e^{-G|z|}}{G},$$

where

$$G \equiv a^2+k_1^2+k_2^2.$$

The χ_3 integration was done by calculating the residues at the poles $\chi_3 = iG$ when $z \geqslant 0$, and $\chi_3 = -iG$ when $z < 0$.

The other integrals of this type are obtained by differentiation with respect to parameter a

$$\iint_{-\infty}^{\infty} e^{i(k_1x+k_2y)} e^{-ar} dxdy = \frac{\partial}{\partial a}\iint_{-\infty}^{\infty} e^{i(k_1x+k_2y)} r^{-1} e^{-ar} dxdy$$

$$= -\frac{\partial}{\partial a}\left(2\pi\,\frac{e^{-G|z|}}{G}\right) = -2\pi\,\frac{\partial G}{\partial a}\,\frac{\partial}{\partial G}\left(\frac{e^{-G|z|}}{G}\right)$$

$$= 2\pi e^{-G|z|}\left(\frac{a|z|}{G^2}+\frac{a}{G^3}\right), \qquad \text{where} \qquad \frac{\partial G}{\partial a} = \frac{a}{G}.$$

$$\iint_{-\infty}^{\infty} e^{i(k_1x+k_2y)} r e^{-ar} dxdy = -\frac{\partial}{\partial a}\iint_{-\infty}^{\infty} e^{i(k_1x+k_2y)} e^{-ar} dxdy$$

$$= 2\pi e^{-G|z|}\left[\frac{a^2|z|^2}{G^3}+\left(\frac{3a^2}{G^4}-\frac{1}{G^2}\right)|z|+\frac{3a^2}{G^5}-\frac{1}{G^3}\right].$$

Therefore, for H we have

$$V_{\mathrm{i}\to\mathrm{f}} \simeq 2\pi C \int_{-s}^{0} e^{ik_3\xi} G^{-1} e^{-G|z|} dz + 2\pi D \int_{-s}^{0} \left[e^{ik_3\xi}(s+z)e^{-G|z|} \left(\frac{a|z|}{G^2} + \frac{a}{G^3} \right) dz \right]$$

$$= 2\pi C e^{-Gs} G^{-1} \int_{-s}^{0} dz + 2\pi D e^{-Gs} \int_{-s}^{0} \left(-\frac{az}{G^2} + \frac{a}{G^3} \right)(s+z)dz = 2\pi C e^{-Gs} s G^{-1}$$

$$+ 2\pi D e^{-Gs} \left[\tfrac{1}{6} \frac{as^3}{G^2} + \tfrac{1}{2} \frac{as^2}{G^3} \right],$$

where the conservation of energy was used: $k^2 = -a^2$, consequently, $G + ik_3 = 0$. For Cs we have

$$V_{\mathrm{i}\to\mathrm{f}} = 2\pi C \int_{-s}^{0} e^{ik_3\xi} \left(\frac{1}{G} - \frac{a^2|z|}{G^2} - \frac{a^2}{G^3} \right) e^{-G|z|} dz$$

$$+ 2\pi D \int_{-s}^{0} e^{ik_3\xi}(z+s)e^{-G|z|} \Big[\frac{a|z|}{G^2} + \frac{a}{G^3} - \frac{a^3|z|^2}{G^3} - a \Big(\frac{3a^2}{G^4} - \frac{1}{G^2} \Big] |z|$$

$$-a \left(\frac{3a^2}{G^5} - \frac{1}{G^6} \right) \Big] = 2\pi C e^{-Gs} \left(-\tfrac{1}{2} \frac{a^2 s^2}{G^2} + \frac{G^2 - a^2}{G^2} s \right)$$

$$+ 2\pi D e^{-Gs} \left[-\tfrac{1}{12} \frac{a^3 s^4}{G^3} + \tfrac{1}{6} \left(\frac{2a}{G^2} - \frac{3a^3}{G^4} \right) s^3 + \tfrac{1}{2} \left(\frac{2a}{G^3} - \frac{3a^3}{G^3} \right) s^2 \right].$$

The probability of the transition between eigenstates per unit of time is given for H by

$$W = \frac{m|k|L^3}{\hbar^3 2\pi^2} \int_0^{2\pi} d\varphi \int_0^{\pi/2} |V_{\mathrm{i}\to\mathrm{f}}|^2 \sin\theta d\theta = \frac{8m|k|e^2}{\hbar^3} N^2 k_v^{-2}$$

$$\left[\int_0^{2\pi} d\varphi \int_0^{\pi/2} k_3'^2 e^{-2Gs} \left[-\frac{Z_{\mathrm{eff}}\, e}{4\pi\varepsilon_0} \frac{s}{G} + \left(\tfrac{1}{6} \frac{as^3}{G^2} + \tfrac{1}{2} \frac{as^2}{G^3} \right) F \right]^2 \sin\theta d\theta. \right.$$

In this expression k_3' and G are functions of θ. We will choose $X = G^2$ as the integration variable. We have $k_3' = k' \cos\theta$ and

$$X \equiv G^2 = a^2 + k_1^2 + k_2^2 = a^2 + k'^2 \sin^2\theta,$$

from which we deduce $dX = 2k_3' \sin\theta \cos\theta$. Finally we obtain

$$W = \frac{4a^4e^2}{\hbar V_0} \int_{a^2}^{a^2+k'^2} e^{-2s\sqrt{X}} \frac{\sqrt{k'^2+a^2-X}}{k'} \left[- \frac{Z_{\mathrm{eff}} es}{4\pi\varepsilon_0 X^{1/2}} + \left(\frac{as^3}{6X} + \tfrac{1}{2} \frac{as^2}{X^{3/2}} \right) F \right]^2 dX,$$

where

$$V_0 = \frac{\hbar^2 k_v^2}{2m}.$$

For Cs we find

$$W = \frac{4a^4e^2}{\hbar V_0} \int_{a^2}^{a^2+k'^2} e^{-2s\sqrt{X}} \frac{\sqrt{k'^2+a^2-X}}{k} \left[- \frac{Z_{\mathrm{eff}}\, e}{4\pi\varepsilon_0} \left(-\tfrac{1}{2} \frac{a^2s^2}{X} + \frac{X-a^2}{X^{3/2}} s \right) \right.$$

$$\left. + \left(-\tfrac{1}{12} \frac{a^3}{X^{3/2}} \right) s^4 + \tfrac{1}{6} \left(\frac{2a}{X} - \frac{3a^3}{X^2} \right) s^3 + \tfrac{1}{2} \left(\frac{2a}{X^{3/2}} - \frac{3a^3}{X^{5/2}} \right) s^2 \right]^2 dX.$$

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