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Electrostatic energy calculation for the interpretation of scanning probe microscopy experiments

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Abstract. We discuss the correct expression for the classical electrostatic energy used while analysing scanning probe microscopy (SPM) experiments if either a conducting tip or a substrate or both are used in the experiment. For this purpose a general system consisting of an arbitrary arrangement of finite metallic conductors at fixed potentials (maintained by external sources) and a distribution of point charges in free space are considered using classical electrostatics. We stress the crucial importance of incorporating into the energy the contribution coming from the external sources (the ‘battery’). Using the Green function of the Laplace equation, we show in a very general case that the potential energy of point charges which are far away from metals is equally shared by their direct interaction and the polarization interaction due to charge induced in metals by the remote charges (the image interaction). When the charges are located close to the metals, there is an additional negative term in the energy entirely due to image interaction. The exact Hamiltonian of a quantum system interacting classically with polarized metal conductors is derived and its application in the Hartree–Fock and the density functional theories is briefly discussed. As an illustration of the theory, we consider an interaction of several point charges with a metal plane and a spherical tip, based on the set-up of a real SPM experiment. We show the significance of the image interaction for the force imposed on the tip.

1. Introduction

Recent progress in the experimental development [1–8] of scanning probe microscopy (SPM) in analysing surfaces of insulating crystals has made it possible to get a deeper insight into the structure of surfaces of real materials and surface processes. However, the interpretation of experimental images is not straightforward, and can be done only in combination with the theory. Usually, the theoretical interpretation of AFM images is based on simple models [9–12] in which the force imposed on the tip originates from the macroscopic long-range van der Waals [13] interaction and a microscopic interaction described using pair potentials between atoms simulating the tip apex and atoms of the sample. In this model only the direct electrostatic interaction between atoms of the tip apex and the sample is accounted for. However, recent applications of scanning tunnelling microscopy (STM) to insulating films grown on metal substrates [14, 15] and combined applications of STM and non-contact atomic force microscopy (AFM) [4, 16, 17] require a more adequate theoretical model in which account is also taken of the polarization of the metal electrodes (i.e. of the tip and the substrate) by the charged atoms of the sample.

Note that, in a typical AFM experiment, the potential on metal electrodes is maintained by external sources (i.e. by the ‘battery’). From the point of view of classical electrostatics [18–21] the polarization of the metals by external charges is caused by the additional potential on the metals due to the charges. This extra potential is compensated by a charge flow from one

electrode to another to keep the potential on the metals fixed. This work is done by the battery. As a result, there will be some distribution of the net charge on the surfaces of metals induced by the point charges in the free space between them. The net charge on each metal electrode would interact with the total charge on other metals and with the point charges. Hereafter, this interaction is called the *image interaction*.

For the interpretation of the non-contact AFM experiments [2–4, 8] one should have an expression for the force imposed on the tip at any time during its oscillations [9–11]. Usually the electrostatic contribution to this force does not include the effect of the sample, i.e. the image interaction, and therefore is a function only of the geometry of the metal–vacuum–metal junction formed by the conducting tip and the substrate and the applied voltage (i.e. a capacitor) [22–28]. In order to calculate the contribution of the image interaction to the force, one has to have the correct formula for the total electrostatic energy of such a system which would include the effect of the image charge, i.e. the effect of the charged particles of the sample on the force imposed on the tip.

It appears, however, that the corresponding general consideration of the electrostatic energy of an arbitrary system of charges and metal conductors is not readily available in the literature. In this paper we offer such a consideration. We discuss possible expressions for this energy and argue that the correct result can be obtained only if the effect of the battery is accounted for in the energy expression. This result is well known [18–21] in the case of a capacitor, i.e. without the effect of the image interaction included. We extend this treatment to this case, especially relevant to the SPM, by incorporating the effect of the sample on the force (i.e. the image interaction) using classical electrostatics (for quantum mechanical treatment of the image interaction see e.g. references [29–44]). This point is considered in detail in section 2. Note that the expression obtained there is more general than the one needed for SPM as the number of metals and their connection via the battery (batteries) do not need to be specified explicitly.

In section 3 we recast the energy in terms of the Green function of the Laplace equation which allows one to arrive at its representation in a very general case and consider its main properties without actually solving the electrostatic problem. We also discuss the exact form of the quantum Hamiltonian operator for a system considered fully quantum mechanically which interacts *classically* with a set of metal conductors taking into account the image interaction. In particular, we show that the correct consideration within the density functional theory (DFT) [45, 46] is hampered by the additional electron–electron interaction via the induced polarization on the metals which should modify the exchange–correlation functional. Note that the general analysis of section 3 goes beyond the topic of the SPM because it sheds new light into the underlying physics of the ‘charge in the external field’ model. In particular, we show that the potential energy $q\phi^{(0)}(\mathbf{r})$ of the charge q in the external potential $\phi^{(0)}(\mathbf{r})$ (produced by some metallic electrodes) is contributed to equally by the direct interaction with the metals and the image interaction. As far as we are aware, this unexpected result has been overlooked up to now in SPM. In addition, we demonstrate that the simple expression $q\phi^{(0)}(\mathbf{r})$ for the energy is not correct if the charges are located close to the metals as, in fact, happens in AFM experiments when the tip comes very close to the sample or/and when the sample is grown on the metal substrate, since at small distances there is a negative correction term U_{im} in the energy. By analysing the asymptotics of the image energy for point charges far away from the metals we find that the correction U_{im} decays as R^{-2} with the distance R from the metals. (We are aware that there is an oscillatory term if the charges (i.e. electrons) are allowed to respond to the external potential and there is a Fermi cut-off (a quantum metal); normally, however, these terms fall off more rapidly than the terms we are discussing [47].)

Finally, in section 4 the theory is applied to a junction formed by a metal plane and

a metal sphere, and the sample is simulated by one or two point charges injected into the junction. It is known [48] that in this case the complete electrostatic problem can be solved exactly, including the effect of the image potential. We improve the numerical efficiency of the solution by keeping a finite number of initial image charges and then summing up analytically the rest of the series. Then, using the correct energy expression derived in sections 2 and 3, we consider the energy of a point charge in the junction as well as a force imposed on the tip with charged and neutral collection of charges between the electrodes, taking fully into account the image interaction. We consider here only a very simple case where the charges are positioned exactly below the sphere along the normal to the plane which passes through the sphere centre. We note, however, that the method outlined in this work can be used in the very general case of arbitrary number of point charges positioned anywhere in space provided that the tip is modelled by a sphere.

2. Electrostatic energy of a system of metals and charges: role of the battery

Consider a set of *finite* metallic conductors of arbitrary shape and an arbitrary distribution of point charges $\{q_i\}$ at the points $\{r_i\}$ anywhere in the free space outside the conductors. We assume that the conductors which will hereafter be designated by indices m, m' are kept at some *fixed* potentials ϕ_m . These potentials are provided by the batteries.

It is known from the standard textbooks (see e.g. references [18–21]) how to calculate the energy accumulated in the electrostatic field \mathbf{E} created by point charges and metals. Using the total energy of the field

$$U = \frac{1}{8\pi} \int_V \mathbf{E}^2 \, dr$$

(the integral is taken over the volume V outside the metals since inside them the field $\mathbf{E} = 0$) and applying the Poisson equation for the field, one gets

$$U = \frac{1}{2} \sum_i q_i \phi(r_i) + \frac{1}{2} \sum_m Q_m \phi_m \quad (1)$$

where the first sum is taken over all point charges whereas the second one is taken over all conductors.

$$Q_m = -\frac{1}{4\pi} \int \int_{S_m} \frac{\partial \phi}{\partial n} \, ds$$

is the charge on the metal m , where the integral is performed over the surface S_m of the metal. Note that the surface integral over a remote surface at infinity (which is surrounding all the metals and the point charges) vanishes due to rapid decrease of the potential to zero there [20]. Therefore, this derivation is not valid for infinite metals for which this assumption is not correct (e.g. a charged infinite metal conductor). We also note in passing that according to classical theory, the charge is distributed at the surface, i.e. it does not penetrate into the bulk of the metal; quantum theory [33–35] gives a certain distribution of the surface charge in the direction to the bulk.

The result of equation (1) has a very simple physical meaning: every charge q at the point r_q (either a point charge outside the metals or the distributed charge on a metal surface) gets energy $\frac{1}{2} q \phi(r_q)$ where the factor $\frac{1}{2}$ is needed to avoid double counting. Note that the potential $\phi(\mathbf{r})$ is produced both by the metals (i.e. by the distributed charges on their surfaces) and by the point charges. Note also that both the potential $\phi(r_i)$ on point charges and the charges Q_m on the metals are unknown and should be calculated by solving the Poisson equation. The effect of the metals comes into play via the boundary conditions and the charges Q_m .

In order to calculate the electrostatic force imposed on any of the conductors, we use the method essentially similar to the one of reference [20] (see section 5) where an arbitrary distribution of metals is considered without point charges. The force is obtained by differentiating the energy with respect to the corresponding position of the metal of interest. It is shown in reference [20] that the same expression for the force is obtained in the cases of fixed potentials or fixed charges on the metals (see also reference [49]). This, however, is not the case if the point charges are present. Indeed, let us move some metal by the vector $\delta\mathbf{r}$. The work $\delta A = -\mathbf{F} \delta\mathbf{r}$ is done by the external force against the force \mathbf{F} imposed on the conductor. When the conductor is moved to the new position, the potential $\phi(\mathbf{r})$ in the system will change by $\delta\phi(\mathbf{r})$. The potential on any metal m will no longer be equal to the fixed value ϕ_m , so there should be some charge flow between the connected conductors to maintain the potential on them. Therefore, some work δA will be spent in changing the potential energy of the field (given by equation (1)) by the amount

$$\delta U = \frac{1}{2} \sum_i q_i \delta\phi(\mathbf{r}_i) + \frac{1}{2} \sum_m \phi_m \delta Q_m$$

and some work δA_b is done in transferring charge *between* the conductors. The latter work δA_b is done by the batteries (as the charge flows via the battery from one conductor to another) and so should be taken with the minus sign: $\delta A = -\delta A_b + \delta U$. Alternatively, one could think of the batteries being incorporated into the system; in that case it would mean that the work done by the batteries would reduce the total potential energy of the whole system.

Let δQ_m be the change of the charge on the conductor m in the process discussed. Then the work $\delta A_b = \sum_m \phi_m \delta Q_m$ (cf. equation (2.5) in reference [20]). Indeed, since $\sum_m \delta Q_m = 0$, this is the work needed to distribute the zero charge initially stored at infinity (where the potential is zero) between different metals by transferring the amounts δQ_m to each metal m . Using the above-given expressions, we obtain

$$\delta A \equiv -\mathbf{F} \delta\mathbf{r} = -\sum_m \phi_m \delta Q_m + \delta U$$

so the final expression for the force imposed on the displaced metal becomes

$$\mathbf{F} = -\frac{\partial U^{eff}}{\partial \mathbf{r}} \quad (2)$$

with the *effective energy* (or the total potential energy of the whole system which includes the batteries as well) defined as

$$U^{eff} = \frac{1}{2} \sum_i q_i \phi(\mathbf{r}_i) - \frac{1}{2} \sum_m Q_m \phi_m. \quad (3)$$

Analogously to (2) an expression is obtained for the force imposed on any point charge: one has to use the same effective energy and differentiate it with respect to the position of the point charge in question. Note also that the calculation of the force is not straightforward: the energy U^{eff} depends on the positions of the metals and the point charges *indirectly* via an unknown potential distribution, $\phi(\mathbf{r})$, and the surface charges, Q_m . We stress that our analysis has been very general: we have not made any specific assumptions concerning the distribution and number of point charges or the number and shape of the metal conductors.

The expression for the effective energy obtained above is similar to that for the potential energy of the field, equation (1). The important difference, however, is in the sign before the sum over the metals which is opposite in the case of the effective energy. This sign, however, makes all the difference. It will be shown in the next section that equation (1) does not give the correct expression for the potential energy of a probe point charge far away from the metals whereas the effective energy, equation (3), does. We will also be able to gain more insight into the physics underlying this simple energy expression by splitting it up into contributions.

3. General consideration of a system of metal conductors and point charges

3.1. A probe charge near a metallic sphere

Before considering a very general case of arbitrary metals and any number of point charges, it is instructive to study first a simple case for which the exact solution exists [19–21].

Let a metal sphere of a radius R_s be kept at a constant potential ϕ_1 and let a point charge q be positioned outside it at a distance $z > R_s$ from the sphere centre. As is well known [19–21], the effect of the sphere can be simulated by a point charge $Q_1^{(0)} = R_s\phi_1$ at its centre and the image charge $q' = -qR_s/z$ at $z' = R_s^2/z < R_s$ inside the sphere on the line connecting the centre and the charge q . The induced charge on the metal sphere is known [21] to be q' and the total potential experienced by q (that is, including the image potential) is

$$\phi(z) = \frac{Q_1^{(0)}}{z} + \frac{q'}{z - z'}.$$

Since the total charge on the sphere is $Q_1 = Q_1^{(0)} + q'$, we get the following expression for the effective energy, equation (3):

$$U^{eff} = C + q\phi^{(0)}(z) + U_{im}. \quad (4)$$

The first term in this expression $C = -\frac{1}{2}\phi_1 Q_1^{(0)} = -\frac{1}{2}\phi_1^2 R_s$ is a constant. In the second term, $\phi^{(0)}(z) = Q_1^{(0)}/z = \phi_1 R_s/z$ is the potential due to the bare sphere itself at the position of the probe charge q . The energy $q\phi^{(0)}(z)$ corresponds to the potential energy of a probe charge q in the external potential of the sphere if the image interaction was switched off. It decays as z^{-1} with the distance from the sphere. The negative third term in equation (4)

$$U_{im} = -\frac{1}{2} \frac{q^2 R_s}{z^2 - R_s^2}$$

decays as z^{-2} and comes exclusively from the image charge. Note that the force, $f = -\partial U^{eff}/\partial z$, imposed on the charge q , can be easily seen to coincide with the well known expression (see e.g. equation (2.11) in reference [21]).

One can also observe that if we ignore the first (constant) term in equation (4), then asymptotically, i.e. far away from the metal sphere, the energy $U^{eff} \sim q\phi^{(0)}(z)$, i.e. it corresponds to the potential energy of the probe charge in the external electrostatic potential of the metal sphere without taking into account the image effects (i.e. the polarization of the sphere by the probe charge q). An interesting point, however, is that the half of this energy comes from the image charge q' . Indeed, the image charge is a part of the total charge Q_1 on the metal, so the part $-\frac{1}{2}\phi_1 q'$ of the second term in equation (3) appears to be equal exactly to $\frac{1}{2}q\phi^{(0)}(z)$. The second part of the energy $q\phi^{(0)}(z)$ at large distances comes from the first term in equation (3) as the direct interaction between the sphere and the charge. This observation clearly demonstrates that the energy $q\phi^{(0)}(z)$ is composed of two equal contributions, one of which does in fact originate from the image charge. Another important observation can be made that the results just discussed can be obtained only from the effective energy, equation (3), *not* from the energy of the electrostatic field given in equation (1). Therefore, part of the energy comes from the work done by the battery which transfers the charge q' from infinity to the sphere. Note that the charge $q' \sim z^{-1}$ and is zero at infinite separation. As the probe charge moves towards the sphere, the charge q' is gradually increased. Note also that at small distances the last term in equation (4) also becomes important.

We note in passing that the case of a charge near a metal plane (i.e. a metal terminated by an infinite plane) can be considered in the limit of a sphere of radius $R_s \gg d$, where $d = z - R_s$ is the distance from the charge to the sphere [21]. The simplest case is when the potential

on the plane is zero. Expanding the energy of equation (4) in terms of small d , one gets that $U^{eff} = -q^2/(4d)$ in the limit of $R_s \rightarrow \infty$ which is a well known result [20].

3.2. General expression of the energy via the electrostatic Green function

It has been shown in the preceding section that the electrostatic energy is represented as the potential energy of the charge in the field due to the bare sphere and a negative correction term which accounts for its polarization. We have found that this result actually holds for arbitrary distances between the sphere and the charge. It appears that it is possible to prove that for an *arbitrary* set of metal conductors interacting with an *arbitrary* arrangement of point charges the electrostatic energy of equation (3) can always be represented by two terms: (i) the energy of the charges in the potential of the bare metal conductors and (ii) the negative image interaction energy, U_{im} , which decays as the inverse square of the distance between the charges and the metals.

Let us start by introducing the formal solution of the electrostatic problem with fixed potentials on metals (the *Dirichlet* boundary conditions) using the Green function of the Laplace equation [21]:

$$\phi(\mathbf{r}) = \sum_i q_i G(\mathbf{r}, \mathbf{r}_i) + \frac{1}{4\pi} \sum_m \phi_m \int \int_{S_m} \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial n'} ds' \quad (5)$$

where $G(\mathbf{r}, \mathbf{r}')$ is the Green function and the second term in the above equation represents a sum of integrals taken over the surface S_m of every metal in the system, with the integrand, $\partial G(\mathbf{r}, \mathbf{r}')/\partial n'$, being the normal derivative of the Green function at the surface taken with respect to its second argument and the direction of the normal \mathbf{n}' directed *outside* the metal. Note that, for the Dirichlet boundary conditions, $G(\mathbf{r}, \mathbf{r}') = 0$ whenever $\mathbf{r}' \in S_m$, and, therefore, it is shown [21] that the Green function is symmetric: $G(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}', \mathbf{r})$.

We stress that the Green function depends only on the *geometry* of the metal conductors but not on the actual potentials ϕ_m on them. It also does not depend on the actual values and positions of the point charges q_i , because the potentials and charges are linearly related. Therefore, all the information about the shape and location of the metal conductors irrespective of their potentials and the polarization induced by the point charges (image interaction) is already contained in the Green function, which makes it an invaluable tool for the present derivation. Note that in practice the Green function can be calculated analytically only for a limited number of cases (one of which is considered in section 4). We will show, however, that our theoretical analysis is valid for *any* Green function, so general conclusions reached in this section will be proven to be correct for *arbitrary* arrangements of metal conductors and charges, i.e. in the very general case.

The expression given above represents the total electrostatic potential at any point \mathbf{r} outside the metals (the self-action of a point charge should be removed when calculating the potential at that point). In order to employ this general result in equation (3), we have to split this potential into contributions. First of all, it is easy to recognize the potential $\phi^{(0)}(\mathbf{r})$ in the second term in equation (5) since it is the only one which does not depend on the point charges:

$$\phi^{(0)}(\mathbf{r}) = \frac{1}{4\pi} \sum_m \phi_m \int \int_{S_m} \frac{\partial G(\mathbf{r}, \mathbf{r}')}{\partial n'} ds'. \quad (6)$$

The Green function in equation (5) can be split into two terms in order to separate the effect of the direct interaction between the point charges from the polarization of the metals:

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \phi_{ind}(\mathbf{r}, \mathbf{r}') \quad (7)$$

where the second part gives rise to the image potential induced by the point charges on the metals:

$$\phi_{ind}(\mathbf{r}) = \sum_i q_i \phi_{ind}(\mathbf{r}, \mathbf{r}_i) = \sum_i q_i \left(G(\mathbf{r}, \mathbf{r}_i) - \frac{1}{|\mathbf{r} - \mathbf{r}_i|} \right) \quad (8)$$

so the total potential

$$\phi(\mathbf{r}) = \sum_i' \frac{q_i}{|\mathbf{r} - \mathbf{r}_i|} + \phi^{(0)}(\mathbf{r}) + \phi_{ind}(\mathbf{r}) \quad (9)$$

The prime on the summation sign means that the self-action of the charge q_i should be removed if $\mathbf{r} = \mathbf{r}_i$. It is easy to see that $\phi_{ind}(\mathbf{r}, \mathbf{r}')$ is the induced potential at the point \mathbf{r} due to a unit point charge at \mathbf{r}' . We also note that the function $\phi_{ind}(\mathbf{r}, \mathbf{r}')$ is *symmetric* because the Green function is symmetric:

$$\phi_{ind}(\mathbf{r}, \mathbf{r}') = \phi_{ind}(\mathbf{r}', \mathbf{r}) \quad (10)$$

It will become clear in section 3.4 that this property appears to be quite useful in formulating an effective Schrödinger equation for a quantum system interacting with the classical metal conductors. Note in passing that the property (10) is an example of various *reciprocity theorems* known in various areas of physics; see e.g. references [18, 21].

Once we know the potential everywhere outside the metals and at their surface, equation (9), expressed via the Green function, we can calculate the charge induced on the metals by the point charges:

$$\delta Q_m = -\frac{1}{4\pi} \int \int_{S_m} ds \frac{\partial}{\partial n} \left(\sum_i q_i G(\mathbf{r}, \mathbf{r}_i) \right). \quad (11)$$

Note that the charge $Q_m^{(0)}$ on the bare metals is calculated using the potential $\phi^{(0)}(\mathbf{r})$ and therefore can also be expressed via the Green function as

$$Q_m^{(0)} = -\frac{1}{(4\pi)^2} \sum_{m'} \phi_{m'} \int \int_{S_m} ds \int \int_{S_{m'}} ds' \frac{\partial^2 G(\mathbf{r}, \mathbf{r}')}{\partial n \partial n'}. \quad (12)$$

Using the expression for the induced charge, δQ_m , given above, the symmetry of the Green function and equation (6), it is easy to check that

$$-\frac{1}{2} \sum_m \delta Q_m \phi_m = \frac{1}{2} \sum_i q_i \phi^{(0)}(\mathbf{r}_i). \quad (13)$$

This is exactly what we have found for the point charge and the sphere in section 3.1. This result holds in the very general case of *arbitrary* arrangement of the metals and point charges: the change of the self-energy of the metal conductors due to the induced charge is equal to minus half the energy of the point charges in the field of the bare metals. We have already seen one example of this identity in section 3.1 when a simple case of a point charge near a conducting sphere kept at a fixed potential was considered. A rather different argument will also be given in the next section where we will demonstrate the validity of equation (13) again by considering an arbitrary system of charges and metals at large separations. Thus, the total electrostatic energy of the system of metals and point charges will then be given by

$$U^{eff} = -\frac{1}{2} \sum_m Q_m^{(0)} \phi_m + U_q + \sum_i q_i \phi^{(0)}(\mathbf{r}_i) + U_{im} \quad (14)$$

where the first term depends exclusively on the mutual geometrical arrangement of all metal conductors and the applied bias and therefore is only important for the calculation of the force

imposed on the metals (e.g. the force on the tip in AFM). Then, U_q is the self-energy of the point charges (their mutual direct interaction), and the image energy given by

$$U_{im} = \frac{1}{2} \sum_{ij} q_i q_j \phi_{ind}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2} \sum_i q_i \phi_{ind}(\mathbf{r}_i) \quad (15)$$

is directly connected to the Green function via equation (7).

This is the central result of this section. We see that the energy of interaction between the point charges and the metals (i.e. excluding the self-energy U_q of the point charges and the first term which is constant for the given geometry of the metals) contains two terms. The first term, $\sum_i q_i \phi^{(0)}(\mathbf{r}_i)$, coincides with the potential energy of the point charges in the external field $\phi^{(0)}(\mathbf{r})$ of the bare metals. We will see in the next section that at large distance R between the charges and the metals it is inversely proportional to R . The second term, U_{im} , given by equation (15), gives a correction to the energy due to image interaction. It will be clear from the consideration of the next section that it decays faster (as R^{-2}).

We expect that the image energy, U_{im} , should be *negative*, as the total electrostatic energy should be lowered due to polarization of the metals. Indeed, let us assume that the metals are kept at zero potential, $\phi_m = 0$. (This assumption will not affect the image energy, equation (15), which depends only on the point charges and the geometry of the metals.) It follows from Thomson's theorem [18] that the electrostatic energy of the field

$$U_V[\phi] = \frac{1}{8\pi} \int_V (\nabla\phi)^2 d\mathbf{r}$$

is a minimum at the exact electrostatic potential $\phi_1(\mathbf{r})$, V being the volume outside the metals. Let us now consider the potential $\phi_q(\mathbf{r})$ corresponding to the same system without metals. Clearly $U_V[\phi_1] < U_V[\phi_q]$. Defining $U_{all}[\phi_q]$ in the same way as $U_V[\phi]$ but with the integration carried out over the whole space including the volume occupied by the metals, we have $U_V[\phi_q] < U_{all}[\phi_q]$, since the integrand is a positive function. Then, in the case of zero potentials on the metals, $U_V[\phi_1] \equiv U^{eff}[\phi_1] = U_q + U_{im}$, since the first and the third terms in equation (14) disappear due to our choice of the boundary conditions. On the other hand, $U_{all}[\phi_q] = U_q$, so we get $U_V[\phi_1] < U_V[\phi_q] < U_{all}[\phi_q]$ or $U_q + U_{im} < U_q$, and so $U_{im} < 0$. Note that one can derive a number of inequalities for the function $\phi_{ind}(\mathbf{r}, \mathbf{r}')$ using the fact that the image energy, equation (15), is negative (e.g. $\phi_{ind}(\mathbf{r}, \mathbf{r}) < 0$, $\phi_{ind}(\mathbf{r}, \mathbf{r}') < \frac{1}{2}|\phi_{ind}(\mathbf{r}, \mathbf{r}) + \phi_{ind}(\mathbf{r}', \mathbf{r}')|$, etc) by considering one, two, etc charges of different sign.

Several points are worth mentioning here. Firstly, the potential energy $\sum_i q_i \phi^{(0)}(\mathbf{r}_i)$ which dominates at large distances between the metals and the charges corresponds to the 'charge in the external field' model. Secondly, this energy is in fact composed of two equal contributions one of which is to do with the image interaction; see equation (13). This should not be surprising at large R , as one of the image contributions to the energy, namely $-\frac{1}{2} \sum_m \delta Q_m \phi_m$, contains the induced charges on metals $\delta Q_m \propto R^{-1}$ which is the same behaviour at large R as for the potential $\phi^{(0)}(\mathbf{r})$ of the bare metals. It is surprising, yet true, that equation (13) actually holds for an arbitrary arrangement of the metals and the charges; this follows from the powerful technique based on the electrostatic Green's function. Thirdly, if we considered the energy of the field, equation (1), instead of the effective energy, equation (3), then we would find it impossible to get the 'charge in the external field' model at all, because the $\frac{1}{2} \sum_m \delta Q_m \phi_m$ and $\frac{1}{2} \sum_i q_i \phi^{(0)}(\mathbf{r}_i)$ terms in the energy would cancel each other. Finally, we note that the consideration given above generalizes the one given in section 3.1 for a charge and a sphere, where it is possible to calculate both the induced charge and the potential explicitly. The derivation of this section does not in fact require that the exact solution is available and is

valid in the case of any arrangement of arbitrary metals and point charges. The only condition which is necessary is that all metals should be finite. This is always met in practice.

3.3. Asymptotics of the electrostatic energy

Consider now an arbitrary set of metal conductors and point charges, the latter being far away from all the metals. This corresponds to the asymptotics of the effective energy, equation (3) or (14). Our consideration will be independent of the one of the previous section. Before the point charges were added to the system, the charges on the metals were [20]

$$Q_m^{(0)} = \sum_{m'} C_{mm'} \phi_{m'} \quad (16)$$

where the coefficients $C_{mm'} = C_{m'm}$ depend on the shape and relative position of the conductors. They form a symmetric square matrix $\mathbf{C} = \|C_{mm'}\|$ which we shall call the *capacitance matrix* for brevity. The potential of bare metals at arbitrary point \mathbf{r} far away from the metals will be asymptotically given as

$$\phi^{(0)}(\mathbf{r}) = \sum_m \frac{Q_m^{(0)}}{|\mathbf{R}_m - \mathbf{r}|} \quad (17)$$

where \mathbf{R}_m is the position of the metal (for points \mathbf{r} which are far away from the metals, the choice of the vector \mathbf{R}_m inside the metal m is not important).

Now we inject into the system a set of point charges q_i at positions \mathbf{r}_i somewhere far away from the metals. Additional charges δQ_m will be induced on the metals which will cause the following change in the potential on them [20]:

$$\delta \phi_m = \sum_{m'} C_{mm'}^{-1} \delta Q_{m'} \quad (18)$$

where $\mathbf{C}^{-1} = \mathbf{C}$ is the matrix inverse to the capacitance matrix. Note that the potential experienced by the metals from the point charges at large distances can be considered as uniform at their surfaces, so equation (18) holds. Since the potential on every metal should not change, the change $\delta \phi_m$ should be compensated exactly by the potential of the point charges:

$$\delta \phi_m + \sum_i q_i R_{mi}^{-1} = 0 \quad (19)$$

where R_{mi} is the distance between the charge q_i and the metal m . Using the last two equations, we can calculate the net charge induced on the metals by the remote point charges as

$$\delta Q_m = - \sum_{m'} C_{mm'} \left(\sum_i q_i R_{m'i}^{-1} \right). \quad (20)$$

Now let us consider the total potential at the point charges. It consists of three parts: (i) the potential equation (17) of the bare metals; (ii) the potential

$$\delta \phi(\mathbf{r}_i) = \sum_m \delta Q_m R_{mi}^{-1} \quad (21)$$

due to polarization of the metals, i.e. due to induced charges on them; and, finally, (iii) the potential due to other point charges. Bearing in mind that the total charge on the metals is $Q_m = Q_m^{(0)} + \delta Q_m$, we can calculate the total energy of the system using equation (3)

$$U^{eff} = -\frac{1}{2} \sum_m Q_m^{(0)} \phi_m - \frac{1}{2} \sum_m \delta Q_m \phi_m + \frac{1}{2} \sum_i q_i \phi^{(0)}(\mathbf{r}_i) + \frac{1}{2} \sum_i q_i \delta \phi(\mathbf{r}_i) + U_q \quad (22)$$

where U_q is the Coulomb interaction energy between charges which is not of interest to us here. Four terms emerge. The first term in equation (22) is a constant for the given geometry of the metal conductors. The second term can be calculated using equation (20) to be

$$-\frac{1}{2} \sum_m \delta Q_m \phi_m = \frac{1}{2} \sum_i q_i \left(\sum_{mm'} \phi_m C_{mm'} R_{m'i}^{-1} \right). \quad (23)$$

The expression in the round brackets here can be rearranged with the help of equations (16) and (17) to give $\frac{1}{2} \sum_i q_i \phi^{(0)}(\mathbf{r}_i)$ for the whole expression (23). This is exactly the same as the third term in equation (22), as expected (cf. equation (13)). Finally, the fourth term corresponding to the image interaction, U_{im} , appears to be given as

$$U_{im} = \frac{1}{2} \sum_i q_i \delta \phi(\mathbf{r}_i) = -\frac{1}{2} \sum_{ii'} q_i q_{i'} \left[\sum_{mm'} R_{mi}^{-1} C_{mm'} R_{m'i'}^{-1} \right] \quad (24)$$

where we have used equations (21) and (20). Thus, at large distances between the charges and the metals, the effective energy is given by the same equation (14) with the potential energy, $\sum_i q_i \phi^{(0)}(\mathbf{r}_i)$, being inversely proportional to the distance R between the charges and the metals, and the image interaction energy, $U_{im} \propto R^{-2}$, decaying faster. Note also that the energy U_{im} is negative as it should be (cf. the previous section). This follows from the structure in the square brackets in equation (24) and the properties of the capacitance matrix [20].

3.4. Exact Hamiltonian for a quantum system interacting classically with metal conductors

Let us consider a quantum system of N electrons (a cluster) which is positioned near a set of metal conductors kept at fixed potentials ϕ_m . For example, this could be a thin insulating crystal film on a metal substrate under a conducting tip of a STM or AFM. It follows from the previous section that the electronic Hamiltonian of such a system in which electrons are interacting *classically* with the metals (as above) is given as

$$\hat{H} = \hat{H}_0^{(N)} - e \sum_{i=1}^N \left[\phi^{(0)}(\mathbf{r}_i) + \sum_A Z_A \phi_{ind}(\mathbf{r}_i, \mathbf{R}_A) \right] + \frac{e^2}{2} \sum_{i,j=1}^N \phi_{ind}(\mathbf{r}_i, \mathbf{r}_j) \quad (25)$$

where e is the charge of the electrons positioned at points \mathbf{r}_i , Z_A is the charge of the atomic core of the atom A of the cluster positioned at the point \mathbf{R}_A and $\hat{H}_0^{(N)}$ is the quantum Hamiltonian of an *isolated* cluster. The second term in equation (25) represents a one-particle interaction of the electrons with the external potential of bare electrodes, $\phi^{(0)}(\mathbf{r})$, and also their interaction with the image potential due to the cores of the cluster. This latter contribution appears without the factor $\frac{1}{2}$ due to symmetry of the function $\phi_{ind}(\mathbf{r}_i, \mathbf{R}_A) = \phi_{ind}(\mathbf{R}_A, \mathbf{r}_i)$. The third term in equation (25) is associated with the interaction between electrons via the polarization of the metals and is a two-particle operator. Note also that there is a diagonal term $i = j$ in the double sum in equation (25) which represents the self-interaction of the electrons via induced polarization.

Using the Hamiltonian operator above, it is easy to derive an effective Schrödinger equation for the cluster. Since we are not going to use this result in this paper, we limit ourselves to the discussion of the total energy of the cluster interacting with the metals. We will also make some general statements, leaving other details to a separate publication. If $\Psi(x_1, \dots, x_N)$ is the electronic wavefunction of the cluster, then the total energy can be written down using reduced density matrices $\rho_1(x; x')$ and $\rho_2(xy; x'y')$ of the first and second orders, respectively

(see e.g. reference [50]):

$$E = \int (\widehat{h}(x)\rho_1(x; x'))_{x' \rightarrow x} dx + \frac{e^2}{2} \int G(x, x')\rho_2(x, x'; x, x') dx dx' + \frac{1}{2} \sum_{A,B} (Z_A Z_B \phi_{ind}(\mathbf{R}_A, \mathbf{R}_B) + V_{AB}) \quad (26)$$

where electronic arguments $x = (r\sigma)$, $x' = (r'\sigma')$ include spin. The first term arises due to a one-particle operator

$$\widehat{h}(x) = -\frac{1}{2}\Delta + \sum_A \widehat{V}_A(x) - e \left(\phi^{(0)}(\mathbf{r}) + \sum_A Z_A \phi_{ind}(\mathbf{r}, \mathbf{R}_A) \right) \quad (27)$$

where $\widehat{V}_A(x)$ is the pseudopotential of the core A , while the second term in equation (26) is associated with the two-particle operator

$$G(x, x') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \phi_{ind}(\mathbf{r}, \mathbf{r}'). \quad (28)$$

Note that it appears to be the electrostatic Green function of equation (7) and, therefore, is symmetric. Finally, the last term in equation (26) describes the core–core interaction, both the direct one, V_{AB} (note that $V_{AA} = 0$), and the indirect one, via induced polarization.

Since the structure of the energy in equation (26) is the same as without metals, it is straightforward to derive e.g. the Hartree–Fock equations [50] for the cluster. An interesting result coming out of this is that the effect of the metals appears in the equations via an additional potential $\phi^{(0)}(\mathbf{r}) + \phi_{ind}(\mathbf{r})$ which is the total net electrostatic potential experienced by an electron because of the metals. This result is the direct consequence of the *symmetry* of the induced interaction, $\phi_{ind}(\mathbf{r}, \mathbf{r}') = \phi_{ind}(\mathbf{r}', \mathbf{r})$, or that of the Green function. The situation is very similar to the one in the theory of point defects in crystals [51, 52] where the quantum cluster interacts with the polarization reaction field of the infinite environment region surrounding it. The reaction field is given by the electrostatic potential of the polarized environment region which is to be calculated self-consistently with the electronic structure of the quantum cluster. Similarly, in the present case of a cluster interacting with the induced polarization of the metals surrounding it, this polarization is accounted for in the cluster equations in the form of the electrostatic potential which is to be calculated self-consistently with the cluster wavefunction.

The direct generalization for the density functional theory (DFT) [45, 46], however, is not straightforward. Indeed, it is *not* enough to add the image energy

$$U_{im} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r})\phi_{ind}(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}')$$

to the density functional (with $\rho(\mathbf{r})$ being the total charge density in the cluster), although one may be tempted to do so, since there will be some additional exchange–correlation term due to the reformulated two-particle interaction operator $1/|\mathbf{r} - \mathbf{r}'| \rightarrow G(x, x')$. Therefore, there is a certain difficulty in DFT in treating the cluster as a quantum system interacting with the classical metals *if* the polarization of metals is to be also included. It is possible, however, to include the metals in the quantum consideration as is done e.g. in references [29, 33, 34, 36–39] where a non-local density functional has been used which is asymptotically equal to the image potential (for quasiparticle treatments and their comparison with the DFT, see e.g. references [30–32, 40]). This implies, in particular, that it is inconsistent to add the image potential to the Kohn–Sham potential [45, 46] while calculating e.g. the effective potential in the STM junction, since this approach does not take into account the self-consistent image potential due to *other electrons*.

4. Point charges on a metal substrate under a conducting tip

As a simple illustration of the above-derived expression (3) or (14) for the electrostatic energy, we now consider a system consisting of a single point charge q positioned between a metal sphere and a metal plane surface with an applied potential difference V (see figure 1). The two electrodes model a metal tip with a spherical apex and a metal substrate as in a real SPM experiment, while the point charge simulates the sample. The metal tip (the upper electrode) is modelled by a sphere of a finite (several hundreds of Å) radius R_s . The lower electrode is also spherical and is considered in the limit of a radius which is much bigger than R_s so that it can be treated as terminated by a planar surface. The total electrostatic energy of such a system, equation (3), is

$$U^{eff} = \frac{1}{2}q\phi(r_q) - \frac{1}{2}Q_1\phi_1 - \frac{1}{2}Q_2\phi_2 \quad (29)$$

where indices 1, 2 refer to the lower and upper electrodes, respectively. One point is now in order. It is easy to see that the energy is defined up to an irrelevant constant which is determined by the choice of the potential at one of the metals. Indeed, let us, for example, move the upper electrode up by Δz . There will be a charge transfer ΔQ between the two electrodes, $Q_1 \rightarrow Q_1 + \Delta Q$ and $Q_2 \rightarrow Q_2 - \Delta Q$, so the change of the last two terms in the energy in equation (29) will be given as $-\frac{1}{2}\Delta Q(\phi_1 - \phi_2) = -\frac{1}{2}\Delta Q V$. In turn, it can be again rewritten simply as $-\frac{1}{2}QV$ by adding another constant, where Q is the total charge on the upper electrode. The first term in the energy, $\frac{1}{2}q\phi(r_q)$, in equation (29) is also defined up to a constant depending on the reference point for the potential. Therefore, without loss of generality, we choose the potential ϕ in the system in such a way that at the lower electrode it is zero (see figure 1).

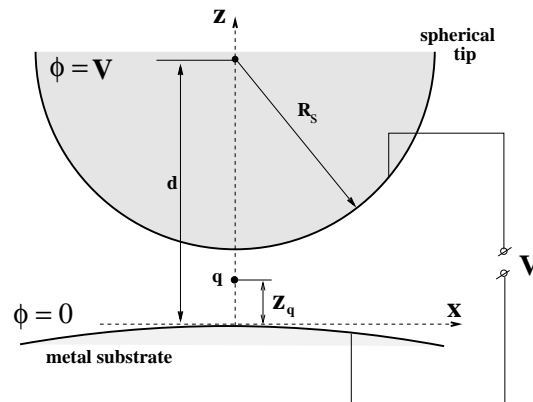


Figure 1. A point charge q between a metal sphere and a metal plane subjected to a bias V .

In order to calculate the energy as a function of the charge and the tip positions with respect to the metal plane, one has to solve the corresponding electrostatic problem. This can be done, for example, by the method of multiple images. Our solution, which is briefly described below, is similar to the one suggested in reference [48]. The main difference is that we have improved the numerical efficiency of the series by considering explicitly only a small number of initial terms and then summing up the rest of the series to infinity analytically. This idea is similar to the one used in reference [53] for the plane–plane junction. Postponing the detailed discussion to the forthcoming publication [54], we will consider here only a very simple case in which

the point charge is positioned along the normal passing through the centre of the upper sphere as shown in figure 1. We then use the method of images to calculate the potential ϕ at the point charge q . This potential consists of two contributions: the potential $\phi^{(0)}$ coming from the bare electrodes and the potential ϕ_{ind} due to image charges induced by the point charge inside the metals.

The solution for $\phi^{(0)}$ can be obtained [55] by starting from a point charge $q_1 = VR_s$ at the sphere centre. This charge provides the potential V everywhere on the sphere surface. To produce the zero potential everywhere on the plane, we introduce multiple images of the charge q_1 in the sphere and in the plane. It is easy to recognize from direct calculation that such a process generates the following sequence of point charges $\{q_k\}$ with $k = 1, 2, \dots$ inside the sphere and above the plane (and the corresponding images $\{q'_k = -q_k\}$ below the plane): $q_{k+1} = q_k/D_k$, where dimensionless $D_{k+1} = 2\lambda - 1/D_k$ with $D_1 = 2\lambda$ and $\lambda = d/R_s$, d being the distance between the sphere centre and the plane (figure 1). The point charges $\{q_k\}$ are all inside the sphere along the normal line passing through the sphere centre. Their z -coordinates are as follows: $z_1 = d$ and $z_{k+1} = R_s(\lambda - 1/D_k)$. Therefore, the potential $\phi^{(0)}(\mathbf{r})$ everywhere between the two metals is given by the point charges $\{q_k\}$ and $\{q'_k\}$ positioned at $\{z_k\}$ and $\{z'_k = -z_k\}$, respectively. The calculation of the potential $\phi^{(0)}(\mathbf{r})$ is facilitated by the fact that the sequence of numbers D_k converges very quickly to a limiting value $D_\infty = \lambda + \sqrt{\lambda^2 - 1}$ which follows from the original recurrent relation above, $D_\infty = 2\lambda - 1/D_\infty$. Therefore, the point charges $\{q_k\}$ converge at the point $z_\infty = R_s\sqrt{\lambda^2 - 1}$ with $q_k \rightarrow 0$ very quickly as $k \rightarrow \infty$, so $\forall k \geq k_0$ (k_0 is of the order of ten) one can position all charges $\{q_k\}$ at z_∞ and all charges $\{q'_k\}$ at $-z_\infty$ and also set $D_k = D_\infty$. Then, the rest of the series for $\phi^{(0)}(\mathbf{r})$ with $k \geq k_0$ can be calculated analytically as two geometrical progressions. This results in just two charges:

$$q_\infty = q_{k_0} + \frac{q_{k_0}}{D_\infty} + \frac{q_{k_0}}{D_\infty^2} + \dots = \frac{q_{k_0}D_\infty}{D_\infty - 1} \quad (30)$$

and $-q_\infty$ to be positioned at z_∞ and $-z_\infty$, respectively, instead of the infinite series of terms with $k \geq k_0$.

The charges $\{q_k\}$ and $\{q'_k\}$ provide the potential V at the sphere and zero at the plane. When the point charge q is injected between the two electrodes at the distance z_q above the plane as shown in figure 1, it produces an additional potential at both the metals. To preserve the boundary conditions, we will build up another sequence of image charges in such a way that the net potential produced by them *and* by q would be exactly *zero* at the two metals (the boundary condition for the Green function; see section 3.2). These new image charges together with the charges due to bare electrodes produce the potential $\phi(\mathbf{r})$ which is the exact solution of the Poisson equation with the corresponding boundary conditions. To fulfil this programme, we first create an image charge $-q$ in the plane. Now the potential at the plane is zero. To make sure that the potential at the sphere is also zero, we create two image charges with respect to the sphere:

$$\xi_1 = -q \frac{R_s}{d - z_q}$$

due to q and

$$\zeta_1 = q \frac{R_s}{d + z_q}$$

due to $-q$; both charges are positioned inside the sphere along the line connecting the charge q and the sphere centre at

$$z_{\xi_1} = d - \frac{R_s^2}{d - z_q} \quad \text{and} \quad z_{\zeta_1} = d - \frac{R_s^2}{d + z_q}$$

respectively. The new image charges ξ_1 and ζ_1 are reflected in the plane; their plane images $\xi'_1 = -\xi_1$ and $\zeta'_1 = -\zeta_1$ produce new image charges ξ_2 and ζ_2 with respect to the sphere, and so on. This process results in two sequences of point charges:

$$\xi_{k+1} = \xi_k \frac{R_s}{d + z_{\xi_k}} \quad \text{and} \quad \zeta_{k+1} = \zeta_k \frac{R_s}{d + z_{\zeta_k}} \quad (k = 1, 2, \dots)$$

which are all positioned inside the sphere along the line connecting the charge q and the sphere centre, their corresponding z -coordinates being

$$z_{\xi_{k+1}} = d - \frac{R_s^2}{d + z_{\xi_k}} \quad \text{and} \quad z_{\zeta_{k+1}} = d - \frac{R_s^2}{d + z_{\zeta_k}}.$$

Note that there are also images of these charges $\{\xi'_k = -\xi_k\}$ and $\{\zeta'_k = -\zeta_k\}$ in the plane. As in the case of the bare electrodes, both sequences of charges $\{\xi_k\}$ and $\{\zeta_k\}$ converge very quickly to the same point z_∞ and their plane images at $-z_\infty$. To facilitate the calculation of the potential, one can sum the explicit contributions from the first $k_0 - 1$ image charges and then sum the geometric progressions of the rest of the series assuming that $\forall k \geq k_0$ the charges ξ_k and ζ_k are all positioned at z_∞ . As in the case of the bare electrodes, this results in the charges

$$\xi_\infty = \xi_{k_0} \frac{d + z_\infty}{d + z_\infty - R_s} \quad \text{and} \quad \zeta_\infty = \zeta_{k_0} \frac{d + z_\infty}{d + z_\infty - R_s}$$

both positioned at z_∞ (and their plane images $\xi'_\infty = -\xi_\infty$ and $\zeta'_\infty = -\zeta_\infty$ positioned below the plane at $-z_\infty$). Therefore, the induced potential $\phi_{ind}(\mathbf{r}) \equiv \phi_{ind}(\mathbf{r}, \mathbf{r}_q)$ ($\mathbf{r}_q = (0, 0, z_q)$) is the vector of the charge q) can be calculated as the potential of $4k_0 + 1$ charges $\{\xi_k\}$, $\{\zeta_k\}$, $\{\xi'_k\}$, $\{\zeta'_k\}$ ($k = 1, \dots, k_0 - 1$), ξ_∞ , ζ_∞ , ξ'_∞ , ζ'_∞ and also $-q$ at $-z_q$. Once we know $\phi_{ind}(\mathbf{r}, \mathbf{r}_q)$ and $\phi^{(0)}(\mathbf{r})$, we can easily calculate the total energy; see equations (14), (15). Note that this solution is exact and is represented in terms of very quickly converging series of point image charges.

Our results for the induced potential, $\phi_{ind}(\mathbf{r})$, are similar to those presented in reference [48]. The contour plot of $\phi_{ind}(\mathbf{r})$ in the case of a single unit charge at $z_q = 3 \text{ \AA}$ in the plane perpendicular to the metal plane and passing through the sphere centre is shown in figure 2. It is seen that the potential has a clear *saddle* character: in the direction perpendicular to the metal plane it has a maximum around $z = 7.75 \text{ \AA}$ and then goes down towards both electrodes demonstrating considerable asymmetry. In the direction parallel to the metal plane, however, the potential smoothly increases to zero in both directions away from the junction. Note that the induced potential for a negative charge q is exactly opposite to the one caused by the positive charge considered above. Note also that the potential $\phi_{ind}(\mathbf{r})$ does not equal zero at the electrodes but is exactly opposite to the potential there of the charge itself, $\phi_q(\mathbf{r})$. Thus, we conclude that a positive (negative) point charge q causes polarization of the metal electrodes which results in lowering (raising) of the electrostatic potential locally near the electrodes.

The total electrostatic energy of the junction at the bias $V = 1 \text{ V}$ as a function of the charge position z_q is shown in figure 3 by the solid line. For comparison, we have also calculated two other quantities: the energies $U_{pot} = q\phi(\mathbf{r}_q) = q(\phi^{(0)}(\mathbf{r}_q) + \phi_{ind}(\mathbf{r}_q))$ and $U_{pot}^{(0)} = q\phi^{(0)}(\mathbf{r}_q)$ which can be naively considered as another possible expression for the potential energy of the charge in the junction. Note that the exact potential at the charge q is used in U_{pot} (which includes the polarization of the metal electrodes by the charge) while in $U_{pot}^{(0)}$ the image charges induced by q are not taken into account and only the potential of bare electrodes is used. The exact potential is negative, has a maximum plateau in the middle of the junction and goes to minus infinity when approaching either of the electrodes. This singular behaviour near the electrodes is the result of the classical consideration of the metals which is valid only some distance (several \AA) from the metals, so interpolation to the crystalline potential inside the

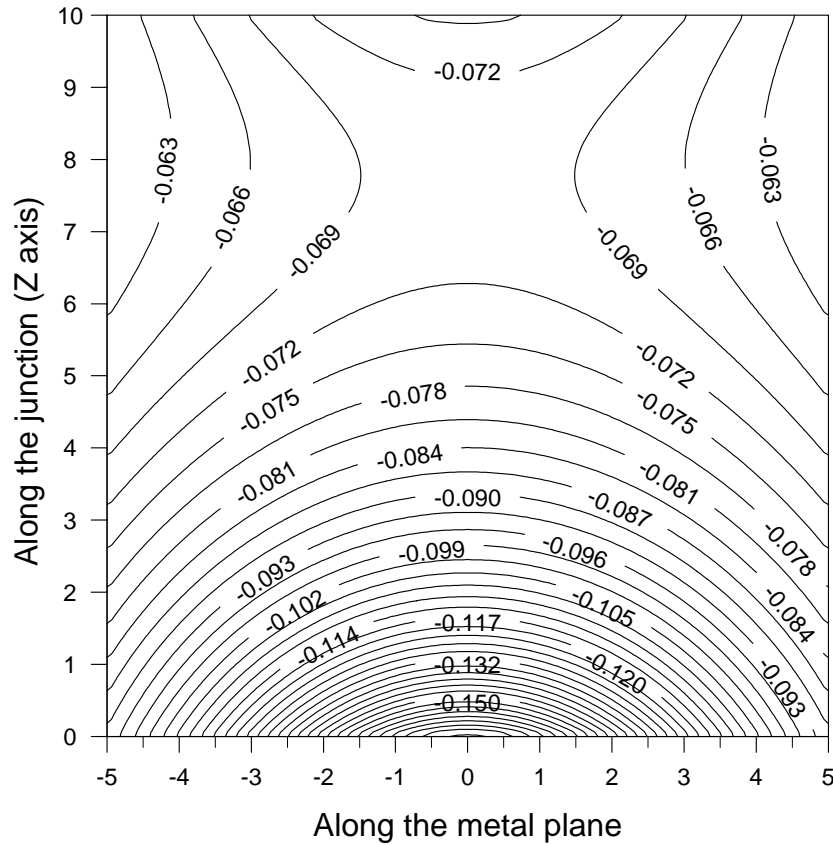


Figure 2. A contour plot of the induced potential (in au) for a positive unit charge in the plane perpendicular to the metal plane. All distances are in Å. Here the sphere radius is $R_s = 200$ Å and the sphere is positioned at $d = 210$ Å above the metal plane, so the gap which opens up along the junction is 10 Å. The metal plane corresponds to $z = 0$ on the plot, while the metal sphere corresponds to $z = 10$ Å.

electrodes on both sides is usually carried out while calculating e.g. the tunnelling current (see e.g. references [56,57]). For rather big R_s and zero voltage the profile of the energy as a function of z_q will be approximately symmetric. The effect of the bias is insignificant and results only in a small lifting of the potential on the right-hand side (at the sphere). Note that this type of behaviour of the potential energy of a unit point charge in the planar–planar junction has been already discussed in the literature [56,58]. One can also see that the approximate energy U_{pot} leads to the correct general behaviour of the energy although it is too high in the middle of the junction. However, $U_{pot}^{(o)}$ appears to be absolutely wrong, stressing the importance of taking into account the effect of the image charge induced on the metals.

To study the effect of the image forces on the tip, we considered four systems:

- (i) bare metal electrodes (i.e. no charges added);
- (ii) one positive unit charge at $z_q = 2.0$ Å;
- (iii) two opposite unit charges at $z_q = 1.9$ Å and $z_q = 2.1$ Å thereby forming a dipole directed along the z -axis; and
- (iv) two positive unit charges at the same positions as in the previous case.

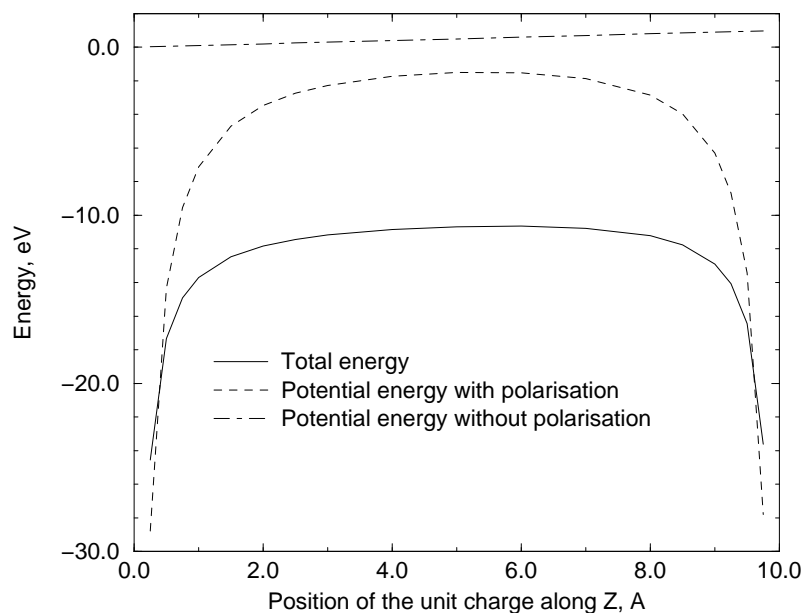


Figure 3. The electrostatic energy (in eV) of a unit point charge as a function of its separation z_q from the metal plane: the exact energy according to either equation (14) or (29) (solid line), the potential energy U_{pot} calculated using the exact electrostatic potential at r_q (dashed line) and the potential energy $U_{pot}^{(0)}$ of the charge calculated using only the potential of the bare electrodes (dot-dashed line). For the parameters of the calculation, see figure 2.

In all cases we used the sphere of $R_s = 200 \text{ \AA}$ and the voltage of $V = 1 \text{ V}$. In the cases of two charges the energy is calculated along the same lines as for a single charge owing to the fact that the induced potential is additive with the number of charges. That is, each point charge will create its own set of image charges inside the sphere and under the plane. The total energy will then be given by equations (14), (15) in which we sum over point charges.

The total energies of either of the systems for various positions $z_{bot} = d - R_s$ of the bottom of the sphere with respect to the metal plane are shown in figure 4. We see that in the case of only one charge the energy is more negative than in the case of the capacitor (i.e. when no charges are added) especially at small distances between the charge and the sphere. The effect becomes even more significant if the second charge of the same sign is added (dot-dashed line). When the two charges are of opposite sign, however, the polarization is highly suppressed (dashed line) and is noticeable only at small distances between the sphere and the dipole.

We have also calculated the force imposed on the tip for the four systems considered above by differentiating their electrostatic energies with respect to the tip position. The results are shown in figure 5. The effect of the polarization of the metal electrodes is clearly visible. For the dipole system (neutral collection of charges in the junction) the force is noticeably different from that calculated without taking into account polarization effects (bare electrodes, solid line) only at very small distances from the charges (less than one \AA) when the classical consideration of the metal polarization is no longer valid [29–35, 38–40, 42]. For the charged sample the force is also significant at intermediate distances from the upper electrode (the force is around 0.3 eV \AA^{-1} even when the bottom of the sphere $z_{bot} = 10 \text{ \AA}$) and non-linearly increases with the charge of the sample.

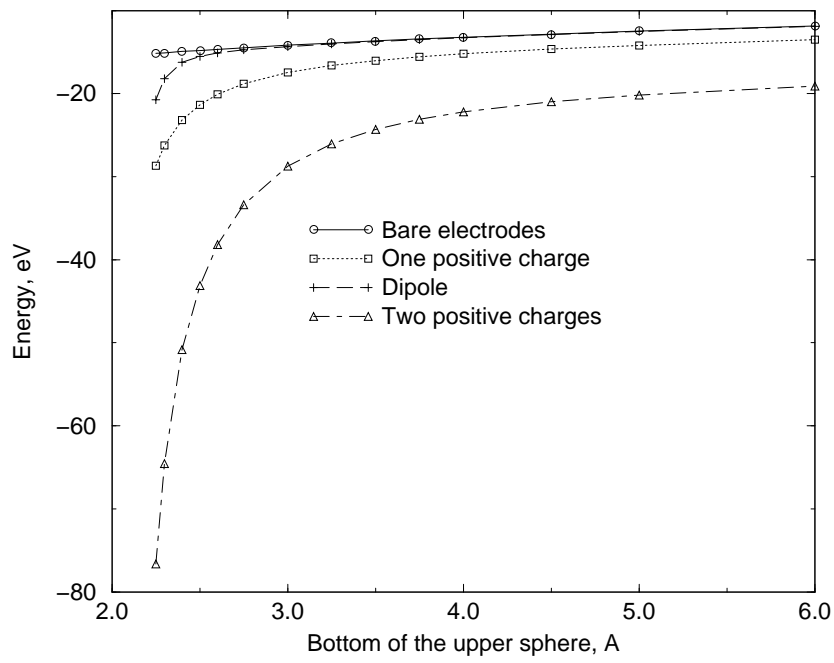


Figure 4. The total energy of the junction without charges (solid line), with one unit positive charge (dotted line), two opposite unit charges (a dipole; dashed line) and with two positive unit charges (dot-dashed line) as a function of the tip position z_{bot} .

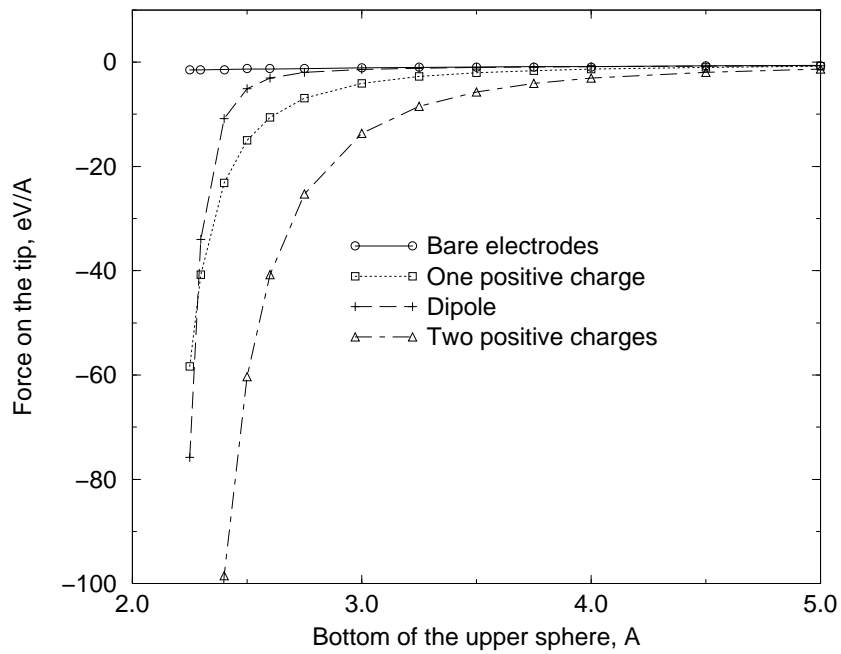


Figure 5. The electrostatic contribution to the force (in eV \AA^{-1}) imposed on the tip. The notation is the same as for figure 4.

5. Conclusions

In this paper we considered the classical electrostatic energy of a system of metal conductors held at constant potentials and point charges outside the conductors. This problem appears e.g. in AFM experiments when a sample is grown on a metal substrate or when a conducting tip is used. We find that in order to calculate the energy correctly, one has to take into account the effect of the battery which maintains the potentials on the metal electrode(s). The resulting energy contains both the energy of interaction of the point charges with the field and the energy of the metal conductors. The metals are polarized by the point charges and therefore have a net distributed surface charge (the image charge) caused by the point charges.

To analyse further the electrostatic energy, we used the Green function of the Laplace equation which allows an elegant and exact (although formal) solution of the electrostatic problem to be written down in the general case. This made it possible to rewrite the energy via the Green function and study its general properties. We find that the contribution of the metals to the energy consists of two terms. The first term which drops as R^{-1} , with the distance R of the point charges from the metals, corresponds to the ‘charge in the external field’ model, i.e. it gives the potential energy of the point charges in the potential of the bare metals without the effect of the image charge. The second term represents a correction to the energy which is to do entirely with the polarization of the metals by the point charges (the image interaction). It is always negative (as indeed it should be for the polarization energy) and dies away as R^{-2} (if there is a Fermi surface, there will also be a faster-falling-off oscillatory term [47]). However, our general analysis revealed that only half of the potential energy of point charges actually comes from their direct interaction with the bare metals, the other half coming from the induced charge on the metals. Therefore, the image interaction appears to be involved in the potential energy of the charge distribution placed in the electrostatic potential of metal electrodes even at large distances between them. At small and intermediate distances the correction term is significant and results in additional lowering of the energy.

Finally, we derived the exact Hamiltonian operator for a quantum system interacting with classical metal conductors. We find that this interaction modifies both the one-particle and the two-particle (electron–electron) interactions in the system by introducing an additional interaction via induced polarization. The derived Hamiltonian allows a simple generalization of the Hartree–Fock (and beyond) method to be applied to the quantum system. However, the application of the method within the DFT is hampered by the necessity to develop a new exchange–correlation functional corresponding to the modified two-electron operator.

As a simple application of the theory, we have considered a conducting tip and a metal plane under an applied bias in order to model the conditions of a real AFM experiment, and then injected into the junction one or two point charges. We used a simple model where the tip is modelled by a *sphere* with a big radius so that the electrostatic problem can be solved exactly for any number of point charges in the junction and, therefore, the effect of the image charge (i.e. the polarization of the metal electrodes by the charge density in the junction) can be studied explicitly. We find that the induced potential digs attractive wells near the electrodes and causes the charge to be unstable there. We also calculated the contribution to the force imposed on the tip itself coming from the induced polarization and found it significant for *charged* systems in the junction. Therefore, we have demonstrated the importance of taking into account the polarization of the metal electrodes while simulating AFM experiments. In particular, this implies that in order to interpret the images obtained in AFM experiments (e.g. in non-contact mode; see references [2, 4, 6, 7, 11]), one has to consider the effect of image forces both on the structure of the sample under study and on the force imposed on the tip. Work on modelling non-contact AFM experiments is now in progress and will be published elsewhere [54].

Acknowledgments

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