Energy gap in tunneling spectroscopy: effect of the chemical potential shift

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We show, that in systems with gapped energy spectra, significant distortions of the differential tunneling conductance curves $\frac{dI}{dV}(V)$ arise in the gap region. The effect depends on the chemical potential and may result in misleading conclusions. We derive an expression for correction of $dI/dV$, which in a number of cases turns out to be significant and assumes positive (at $V < 0$), as well as negative (at $V > 0$) values. The correction to $dI/dV$ associated with the chemical potential shift has a nearly linear dependence on the tip-sample separation $z$ and vanishes at $z \to 0$.

INTRODUCTION

Scanning tunneling spectroscopy (STS) is widely used for study of energy structure of atomically clean surfaces of solids with spatial resolution down to the atomic level. In many cases the question of presence of an energy gap in the energy spectrum of the surface states plays a crucial role. For instance, two-dimensional electron gas on the surfaces of semiconductors [1, 2], monolayers of various layered materials (as a review see [3]) superconductor surfaces [4] and especially the topological insulators [5] are examples of objects where STS may help to distinguish between different possible surface phases. As the surface properties are usually affected by numerous parameters such as, for example, the synthesis conditions, substrate doping, or presence of adsorbate affecting the doping level of the surface states, the question on the effect of the chemical potential level on STS results is also of great interest.

In the scanning tunneling spectroscopy the differential conductance, $dI/dV$, of the tunneling junction (sometimes normalized by $I/V$) is used as a measure for the local density of states (LDOS) $\rho_s(eV)$ (see, for example, [6–10] and references therein). LDOS is usually considered to be proportional to the differential tunneling conductance, $\rho_s(eV) \propto dI/dV$, and, consequently, nonzero $dI/dV$ indicates nonzero $\rho_s(eV)$ and vice versa. In practice, however, this method leads to contradictory results. In some cases, such as superconductors, the energy gap region does correspond to zero differential tunneling conductance (up to thermal smearing). In other cases, e.g., in the $\text{Bi}_2\text{Se}_3$ topological insulator, tunneling spectroscopy of atomically clean surfaces doesn’t yield zero $dI/dV$ at the Dirac point [11], moreover the values in this point, obtained on different samples, differ significantly (see, e.g., [12]).

It is however known, that the relation $\rho_s(eV) \propto dI/dV$ holds with finite precision, and a vast amount of literature is dedicated to the recovery of $\rho_s(E)$ from $I(V)$ tunneling characteristics (see [13–15] and references therein).

For the purposes of the present work it is enough to consider a simple model [16] of a planar tunneling junction conductance in the trapezoidal barrier approximation. Numerous refinements of this model, taking into account image charges, tunneling probe shape and other factors (see, e.g., [4, 10, 13]), don’t change the conclusions of the present work essentially.

Tunneling current in the framework of this model is given by

$$ I = A \int_{-\infty}^{\infty} \rho_s(E)\rho_t(E - eV)T(E, V, z) (f(E - eV) - f(E)) dE, $$

where $\rho_s(E)$ is the density of states of the probe, $T(E, V, z)$ is the tunneling barrier transmission, $f(E)$ is the distribution function.

For the sake of simplicity let $e \equiv 1$, and let us consider the case of zero temperature. Then the expression for the tunneling current (1) becomes

$$ I = A \int_{0}^{V} \rho_s(E)\rho_t(E - V)T(E, V, z) dE, $$

and for the differential conductance we have:

$$ \frac{dI}{dV} = A\rho_s(V)\rho_t(0)T(V, V, z) + A \int_{0}^{V} \rho_s(E) \frac{\partial}{\partial V} [\rho_t(E - V)T(E, V, z)] dE. $$

Here the first term is directly connected with the local density of states, but contains $T(V, V, z)$ as a factor, which depends on $V$ and strongly depends on $z$. In the simplest case the dependence of $T$ on $V$ is neglected, by assuming $T = e^{-\kappa z}$, and $dI/dV$ is normalized by $T$ or simply by the value of $dI/dV$ at a particular point. Often to take into account the dependence of $T$ on $V$ the normalization by $I/V$ is used. Such a normalization may lead to divergences at edges of the energy gap in case of a gapped LDOS, so in such cases $I/V$ is averaged over an interval $\Delta V$ [17]. Writing the equation (1) in a symmetrical form with respect to the tip and the sample, Ukrainsev proposed using $F = A_tT(V, V, z) + A_sT(0, V, z)$ for normalization. This method yields the density of unoccupied states of the sample at positive $V$ and the density of unoccupied states of the tip at negative $V$ [13]. The second term in (2) is a contribution, brought about by the change of the barrier transmission with applied voltage, as well as by a non-constant density of states of
the probe. In practice this term is considered small or a smooth background, insignificant in determination of peak positions in the LDOS, and consequently dropped. A more accurate determination of $\rho_s(E)$, this term, is the subject of a number of papers, e. g. [13,14]. Koslowski et. al. [14] using the WKB approximation for a trapezoidal barrier reduced the problem to a set of integral equations and proposed an iterative procedure to solve it. The WKB parameters estimation and effects of non-constant tip density of states are analyzed in the work of Passoni et. al. [13].

We are interested in the differences in tunneling conduction spectra (besides a shift in voltage), arising in otherwise identical systems with different chemical potential of the sample. From equation (2) it follows, that if the chemical potential position doesn’t fall outside the energy gap, both the current, and it’s correction are equal to 0 and the presence of a gap in the density of states is correctly determined by STS. This fact explains, for example, successful use of tunneling spectroscopy in superconductor studies, where the gap is opened on the Fermi level. As we show below, a completely different situation may arise in the study of semiconducting surfaces, where the chemical potential can assume different values and be outside the energy gap.

In the present work we analyze the effect of the chemical potential position of the sample on the differential tunneling conductance. We show, that the effect of the chemical potential shift doesn’t come down to just a voltage shift of the $\frac{dI}{dV}(V)$ curves. We derive an expression for the correction to the tunneling junction conductance, which in a number of cases turns out to be significant and assumes positive (at $V < 0$), as well as negative (at $V > 0$) values. A method of identification and elimination of this correction on the basis of analysis tip-sample separation dependence is proposed.

**EFFECT OF THE CHEMICAL POTENTIAL SHIFT**

Let us consider the conditions under which such a nonzero correction emerges and how it affects STS results obtained at different chemical potential values. For this purpose we calculate the change in the differential tunneling conductance if the chemical potential is shifted by $\delta\mu$.

Consider two identical systems, different in the value of the chemical potential only (Fig. 1). The parameters of these systems are related as follows:

\[
\begin{align*}
\tilde{E} &= E - \delta\mu, \\
\tilde{V} &= V - \delta\mu, \\
\phi_t &= \phi_s - \delta\mu, \\
\rho_t(\tilde{E}) &= \rho_s(E), \\
\rho_t(\tilde{E} - \tilde{V}) &= \rho_t(E - V), \\
\tilde{T}(\tilde{E}, \tilde{V}) &= T(E, V),
\end{align*}
\]

where $\phi_t$ and $\phi_s$ are the work functions of the tip and the sample correspondingly. Tunneling current in the second system can be expressed through the tunneling current in the first one:

\[
\tilde{I} = I - A \int_0^{\delta\mu} \rho_s(E) \rho_t(E - V) T(E, V, z) dE.
\]

Note, that the difference between the currents is associated only with states with energies between the chemical potential levels of the two systems. After differentiating we obtain

\[
\frac{d\tilde{I}}{d\tilde{V}} = \frac{dI}{dV} - A \int_0^{\delta\mu} \rho_s(E) \frac{d\rho_t(E - V)}{dV} T(E, V, z) dE - A \int_0^{\delta\mu} \rho_s(E) \rho_t(E - V) \frac{\partial T}{\partial V}(E, V, z) dE.
\]

It is evident that the chemical potential shift results not only in a voltage shift of the differential conductance curve $G(V)$ by $\delta\mu/e$, but also in the appearance of an additional contribution $\Delta G$, changing the value of $dI/dV$. This contribution contains a part, associated with a non-constant tip density of states, and a part, caused by the change of the tunneling barrier transmission with applied voltage. Let’s focus on the latter by assuming $\rho_t \equiv 1$. Then

\[
\Delta G = -A \int_0^{\delta\mu} \rho_s(E) \frac{\partial T}{\partial V}(E, V, z) dE. \tag{3}
\]

Note that since $\frac{\partial T(E, V, z)}{\partial V} \leq 0$, the sign of $\Delta G$ coincides with the sign of $\delta\mu$.  

![FIG. 1: Energy diagrams of two tunnel junctions with different chemical potential of the sample.](image-url)
Let us now consider the effect of this correction on the STS results on some examples.

**EXAMPLES**

We use the WKB approximation for the trapezoidal barrier on Fig. 1 for our calculations:

\[
T = \exp \left( -\frac{2\sqrt{2m}}{\hbar} \sqrt{\phi + \frac{V^2}{2} - E} \right)
\]

and

\[
\frac{\partial T}{\partial V} = -\frac{z}{2\hbar \sqrt{\phi + \frac{V^2}{2} - E}} T,
\]

where \(\phi = \frac{\phi_s + \phi_t}{2}\) is the average work function of the tip and the sample. Substituting (4) into (3) and assuming that \(V \ll \phi\) and the barrier transmission varies weakly on the scale of the gap in the density of states, we obtain an approximate expression for

\[
\frac{dI}{dV} \approx \left( \rho_s(V) + z \sqrt{\frac{m}{2\hbar^2 \phi}} \int_{0}^{\mu} \rho_s(E) dE \right) A T,
\]

which may be used to evaluate the correction.

**V-shaped LDOS**

We begin our analysis with a V-shaped density of states, shown in Fig. 2(a). Such a behavior exhibits a LDOS in the vicinity of the Dirac point of the surface states in 3D topological insulators. We still assume the temperature to be 0, tip density of states to be constant, and we measure the value of the chemical potential from the minimum of the LDOS (i.e., from the Dirac point in the case of 3D topological insulators).

In Fig. 3 a set of \(\frac{dI}{dV}(V)\) curves is shown modeled under these assumptions at different \(\delta\mu\). \(\frac{dI}{dV}(V = 0)|_{\delta\mu=0} = 0\) in agreement with the usual interpretation of STS results. However when the chemical potential shifts into the conduction band the value of the differential tunneling conductance at the minimum of the density of states grows and is not zero anymore, while when the chemical potential shifts into the valence band we observe negative differential conductance at the minimum of the sample LDOS, which in scanning tunneling spectroscopy is often considered a sign of poor quality of the tunneling probe. We also note, that the effect is significant and the apparent density of states may constitute a sizable fraction of the LDOS outside the gap. Obviously normalization by \(I/V\) doesn’t lead to the disappearance of the effect, as is evident from Fig. 3(b).

The dependence of \(\frac{dI}{dV}(\delta\mu)\) at the minimum of the LDOS \((eV = -\delta\mu)\) on the chemical potential shift \(\delta\mu\) is shown in Fig. 4. It is evident that this dependence is nonlinear, has a slope reduction in the region of reduced density of states, and outside the V-shaped gap the dependence is stronger.
Gapped LDOS

Let a gap opens in our V-shaped spectrum as in Fig. 2(b). Such a density of states corresponds, for example, to a dielectric surface of a semiconductor, or a surface of a thin layer of a topological insulator where topological protected surface states of opposite surfaces hybridize. A set of tunneling spectra modeled for such a LDOS is shown in Fig. 5. One can see, that zero density of states in the gap corresponds to nonzero differential tunneling conductance: positive if the chemical potential is in the conduction band (which might be incorrectly interpreted as appearance of states inside the energy gap) and negative if it lies in the valence band (which might be incorrectly interpreted as a bad tunneling probe). Negative differential conductance was observed in tunneling experiments on thin organic films and was attributed among other reasons to the change in the barrier transmission [18].

As in the case of V-shaped density of states, the normalization of the tunneling spectra $dI/dV$ by $I/V$ (Fig. 3b)) doesn’t eliminate the correction. We also note a small tilt in the gap region on the $dI/dV(V)$ and $d\ln I/d\ln V$ curves if the chemical potential is outside the gap, the sign of the tilt being opposite for $dI/dV(V)$ and $d\ln I/d\ln V$. The presence of such a tilt can be regarded as an indicator of a nonzero $\Delta G$. As expected, zero density of states in the gap region corresponds to zero differential tunneling conductance only if the Fermi level lies inside the gap.
FIG. 7: The value of $dI/dV$ at the LDOS minimum (Fig. 2(b)), normalized by $dI/dV$ at the gap edge, at different tip-sample separations and chemical potential shifts.

Dependence of $\Delta G$ on $z$

As is evident from Figs. 4, 6, the relative value of the correction depends on the distance between the probe and the sample. This dependence at different chemical potential positions is shown in Fig. 7. In accordance with equation (4) the correction to $dI/dV$ diminishes largely linearly with the tip approaching the sample surface, with $\lim_{z \to 0} \Delta G = 0$. This property may be used to establish the fact of the presence of the contribution (4), but also for its minimization or practically full elimination.

CONCLUSION

Thus, the dependence of the tunneling barrier transmission on applied voltage can result in an additional contribution to the differential conductivity of the tunneling junction in the energy gap region. If in a tunneling $I(V)$ curve measurement the gap edge is reached at a nonzero value of tunneling current, a change in tunneling barrier transmission with voltage leads to a change in tunneling current and a nonzero slope $dI/dV$, which in the usual approach is interpreted as nonzero density of states. In particular, this may explain substantially different values of normalized differential conductivity in the Dirac point of the surface states of Bi$_2$Se$_3$ topological insulator in tunneling spectra (see, e.g., [12]). Another example is the study of surface states on semiconductors with low temperature scanning tunneling microscopy and spectroscopy. Common practice in this case is usage of highly doped degenerate semiconductors, since current carriers in them don’t freeze out. This is a kind of systems where we can expect a significant contribution from the corrections, associated with the chemical potential shift beyond the energy gap in the density of states. To identify this contribution and eliminate it one can use almost linear dependence of its normalized value on the tip-sample separation. On the other hand, if the gap opens on the Fermi level, as it occurs in superconductors, quasi-one dimensional conductors with charge or spin density waves and systems with Coulomb blockade, such an addition to the zero value of differential tunneling conductance does not emerge.

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