Comment on "Signature of a Chemical Bond in the Conductance between Two Metal Surfaces"

In a recent Letter [1], Hofer and Fisher proposed a linear dependence of the tunneling current on the interaction energy with a universal constant

$$\Delta I_{\mu\nu}\ [\mathrm{nA}] \approx (8e/h)\Delta E_{\mu\nu} \approx 3.1 \times 10^5 \Delta E_{\mu\nu}\ [\mathrm{eV}], \quad (1)$$

and claimed being verified by the STM experiments in Ref. [2] in the low-conductance regime.

Equation (1) cannot be valid. Qualitatively, tunneling current is proportional to bias voltage, which has no universal relation with interaction energy. Quantitatively, even for a single pair of states, the tunneling current predicted by Eq. (1) is much too big. The huge discrepancy is in part due to a *severe underestimate* of the interaction energy: in both [1,3], *only* a second-order perturbation term was taken into account.

A perturbative treatment similar to Bardeen's tunneling theory shows that the dominant part of the interaction energy between a tip state χ and a sample state ψ is a first-order term [4],

$$\Delta E_{\mu\nu} = \pm|M_{\mu\nu}|, \quad (2)$$

mathematically identical to Bardeen's tunneling matrix element $M_{\mu\nu}$. For a pedagogical derivation, see [5]. Identity (2) infers an experimentally verifiable equation between tunneling conductance G and interaction energy ΔE [4]:

$$G \approx G_0 \rho_S \rho_T |\Delta E|^2. \quad (3)$$

Where $G_0 = 2e^2/h$ is the conductance of a single-atom contact, ρ_S and ρ_T are the Fermi-level density of states of the sample, and the tip, respectively. Eq. (3) is verified explicitly in Ref. [2]. The value of $\rho_S \rho_T$ thus obtained agrees well with theoretical expectations [2].

In the low-conductance regime, the force F varies slowly with tip-sample separation z, reportedly behaves like $F \propto I^{1/4}$, even slower than a quadratic relation [2]. The slow variance is due to the presence of the van der Waals force, which varies as z^{-2}. See Fig. 1(a). First, by fitting the tunneling current data with

$$I = I_0 e^{-2\kappa z}, \quad (4)$$

one obtains $\kappa \approx 6.55\ \mathrm{nm}^{-1}$ and $I_0 \approx 7200$ nA. The bias is 100 mV. At $z = 0$, $G \approx 72\ \mu$S, very close to the theoretical value of G_0, 77.84 μS. Therefore, the origin of z was accurately determined in Ref. [2]. The observed force is a sum of van der Waals force and chemical-bond force [4,6],

$$F = -Az^{-2} - Be^{-\kappa z}. \quad (5)$$

A least-squares fit yields $A = 0.295\ \mathrm{nN\,nm}^2$ and $B = 260$ nN. Using the estimated tip radius, 2.5 nm [2], the Hamaker constant is found to be 4.3 eV, consistent with textbook values [6]. From B and I_0, we find $\rho_S \approx \rho_T \approx 0.05$ states per eV, which is reasonably accurate [2].

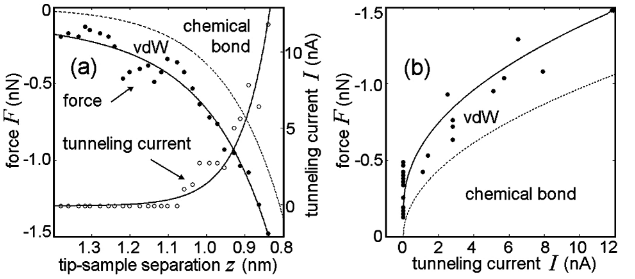

FIG. 1. (a) Force and tunneling current in the low-conductance regime. Experimental data points are taken from Fig. 1 of Ref. [2]. The same data are replotted in Fig. 5 of Ref. [2] for verifying Eq. (3), purposely in F^2 vs I format. In the low-conductance regime, the data points of F are squeezed to nearly zero. See Fig. 1 in the Reply. Plot (b) shows the original data in F vs I format. Dotted curve delineates the chemical-bond force from the van der Waals force.

In Ref. [2], the data in Fig. 1 are replotted in Fig. 5. Designed for verifying Eq. (3), it was plotted purposely in F^2 vs I format. See Fig. 1 in the Reply. The original data, in F vs I format, is shown here in Fig. 1(b). The solid curve is derived from Eqs. (4) and (5),

$$F = -A[2\kappa/(\ln I_0 - \ln I)]^2 - B\sqrt{I/I_0}. \quad (6)$$

Again, clearly the relation between F and I in the low-conductance regime is far from linear.

It is noteworthy that Ref. [7] did not report any experimental observation of a linear relation between tunneling current and force at all. The statement in the Abstract, "Close correlation between conductance and interaction forces in an STM configuration was observed," makes readers wonder whether the authors of Ref. [7] favor Eq. (1) or Eq. (3).

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