

**Hofer and Fisher Reply:** In our Letter [1] we introduced a linear relationship between current and interaction energy, which has subsequently been proven on the basis of scattering theory [2]. The underlying idea is that the interaction between atoms of a metal surface and the STM tip is due to the transfer of electrons; while covalent bonding is due to oscillations of electrons, tunneling current is unidirectional. The probability of electron transfer is in both cases determined by the geometry of the tunneling junction and the band structure of the surface and tip. Chen previously presented [3] a different relationship between current and interaction energy based on the same basic notion. To derive a relation between interaction energy and tunneling current he compared a tunneling junction and a hydrogen molecular ion [3]. However, since the atomic  $1s$  states are degenerate, the tunnel splitting is not a small parameter, as assumed in the comparison. The difference between his original relation and our derivation is due to this omission.

Regarding Eq. (7) in [1], the current  $\Delta I_{\mu\nu}$  refers to the rate at which the tunneling perturbation transfers charge from state  $\mu$  to state  $\nu$ , or vice versa. For the vast majority of pairs  $(\mu, \nu)$  these two contributions cancel out; only if the applied bias is such that one state is filled, and the other empty, does a net current flow. The net flow measured in a STM is a very small fraction (of the order  $10^{-4}$  to  $10^{-5}$ ) and does of course depend on the bias voltage. There is therefore no *universal* relation between the interaction energy and the *measured* tunneling current. However, given a preset bias voltage, the relationship will be linear over the whole distance range where perturbation theory is applicable. This was demonstrated in the same Letter [1] by first-principles simulations; it has also been convincingly established by subsequent high-precision experiments (e.g., [4]).

The theoretical derivation of the linear relationship between tunneling current and interaction energy in [2] is based on the nonequilibrium Keldysh formalism. The scattering formalism leads to a modification of the standard Bardeen approach. To first order in the Dyson series, we derive an additional term, which depends quadratically on the bias voltage, in line with experiments [2]. The same derivation allows us to determine the interaction energy between the two leads in the low coupling regime. Here, we find a dependency of the energy on all tunneling transitions, equivalent to Eq. (7) in [1].

The measurements of Schirmeisen *et al.* [5], far from supporting a *quadratic* relationship between current and interaction energy or forces, actually show that the relationship is *linear* up to about 20 nA (i.e., throughout the region where perturbation theory is expected to be valid), and deviates only above this range. The *quadratic* fit in the range above 20 nA is quite poor, while a linear fit below 20 nA is close to perfect. The original figure is shown below (Fig. 1). We have also plotted the square of the

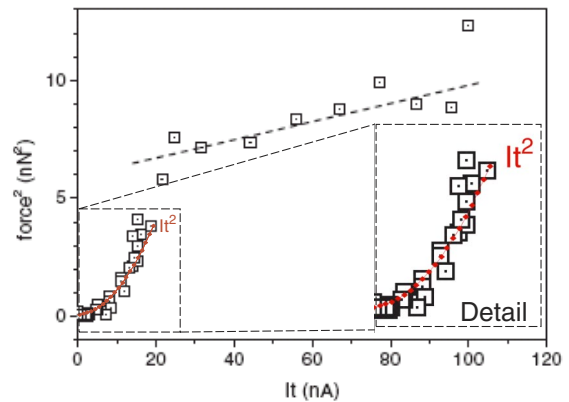


FIG. 1 (color online). Figure 5 of the measurements by Schirmeisen *et al.* [5]. The square of the current in the low current regime is included (see detail). The curve fits the experimental  $F^2$  values very well in the range below 20 nA.

tunneling current  $I_t^2$  up to 20 nA; the proportionality constant is roughly  $0.01(N/A)^2$ : this curve reproduces the increase of the attractive forces in the low current regime very well.  $I_t^2$  is thus experimentally proportional to  $F^2$ , the relation between current and force must be linear:  $I_t \propto F$ . That attraction in the low-conductance regime is due to van der Waals interactions, as claimed in Chen's Comment [6] (see Fig. 1b of the Comment), can be excluded from experimental evidence: van der Waals interactions do not depend on the lateral position of the tip relative to surface atoms; they can therefore not be related to the change of the tunneling current in high-resolution scans.

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- [1] W. A. Hofer *et al.*, Phys. Rev. Lett. **91**, 036803 (2003).
- [2] K. Palotas *et al.*, J. Phys. Condens. Matter **17**, 2705 (2005).
- [3] C. Julian Chen, *Introduction to Scanning Tunneling Microscopy* (Oxford University, New York, 1993).
- [4] G. Rubio-Pollinger *et al.*, Phys. Rev. Lett. **93**, 116803 (2004); S. Hembacher *et al.*, Phys. Rev. Lett. **94**, 056101 (2005); Y. Sun *et al.*, Phys. Rev. B **71**, 193407 (2005).
- [5] A. Schirmeisen *et al.*, New J. Phys. **2**, 29 (2000).
- [6] C. Julian Chen, preceding Comment, Phys. Rev. Lett. **96**, 069701 (2006).