

# Bardeen's tunneling theory as applied to scanning tunneling microscopy: a technical guide to the traditional interpretation

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## Abstract

This article is a thorough tutorial on the traditional approach to Bardeen's tunneling theory in the context of scanning tunneling microscopy. We follow C. B. Duke's interpretation of Bardeen's theory as the tunneling analog of Oppenheimer's perturbation theory for field ionization of atomic hydrogen. We explain Oppenheimer's ideas, Fermi's Golden Rule, and Bardeen's formulas; and we derive the celebrated Tersoff-Hamann formula using an argument due to C. J. Chen. Finally, we discuss the application of Bardeen's theory to scanning tunneling microscopy beyond the Tersoff-Hamann approximation.

## 1 Introduction

Scanning tunneling microscopy can produce atomic resolution images of metallic or semiconductor surfaces by making electrons tunnel between a metallic probe (the tip) and the surface undergoing the scan (the sample). The tip is attached to piezoelectric crystals which, with the help of electronic feedback control, can position the tip precisely relative to the sample beneath it. During the scan, the tip is ordinarily kept between 5 and 15 Ångstroms away from the

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sample (measuring the distance from the nucleus of the apex atom of the tip to the nucleus of the sample atom). The tip and sample are maintained at different voltages, urging an electronic current to flow through the “tunneling barrier” between them. Typically, the tunneling currents are in the nanoampere range (say  $0.1 - 5\text{nA}$ ) and the voltage applied across the barrier ranges from  $10\text{mV}$  to  $10\text{V}$ .

The invention of the Scanning Tunneling Microscope (STM) in 1981 was preceded by two technological achievements: the invention of the topografiner by Young *et al.* in 1972, and the electron tunneling experiments reported by Teague in his Ph.D. dissertation in 1978 [1]. The topografiner was a device that used a piezoelectric driver to scan a surface whose probe rested approximately  $100\text{nm}$  above the sample surface. Using a field emission current induced by applying a positive voltage of a few  $\text{kV}$  to the sample, the topografiner could produce a surface image with a lateral resolution of  $400\text{nm}$  [2]. Teague’s experiments demonstrated vacuum tunneling between two gold electrodes, at voltages and tunneling gap widths used in modern day STMs. Teague’s apparatus allowed fine adjustment of the gap width, but did not have a raster scan mechanism [3]. Binnig and Rohrer combined these technologies to create the STM [4]. They used the STM to determine the atomic positions in  $\text{Si}(111)\text{-}7\times 7$ , one of the most complex surface reconstructions, highlighting the STMs ability to image at the atomic scale [5].

The resolution of STM images depends on the shape of the tip; atomic resolution is possible when a single atom of the tip is nearer to the sample than all other tip atoms. This effect is due to the fact that the probability of tunneling through a high barrier decreases exponentially with the width of the barrier, so that the tunneling current mainly flows across the narrowest parts of the barrier. The exponential dependence of tunneling on barrier width in the weak tunneling regime can be confirmed by examining the exact solution of a simplified tunneling problem, e.g., plane waves tunneling through a square barrier (see Section 3.2.1 of [6] for a detailed calculation).

The pre-eminent quantitative theory of the tunneling current in scanning tunneling microscopy is based on J. Bardeen’s theory [7]. Bardeen’s tunneling theory was published in 1961 and applied to the scanning tunneling microscope in 1983 by Tersoff and Hamann [8]. The predictions of Bardeen’s theory are considered to be trustworthy when the tip and sample are sufficiently far apart, and when the bias (i.e., the potential difference between the tip and

the sample) is low enough. This will be discussed in Section 4.

The way to derive Bardeen’s tunneling theory is not straightforward; it does not proceed by routine application of textbook techniques.<sup>1</sup> There are two approaches to Bardeen’s theory: the approach using nonequilibrium Green functions, and the “traditional” approach (our name). The traditional approach to Bardeens’ theory is due to C. B. Duke [19], who observed that the theory is analogous to Oppenheimer’s theory of field ionization of hydrogen [20]. But Oppenheimer’s “perturbation” theory is peculiar: it differs conceptually from standard time-dependent perturbation theory familiar from textbooks, and it is inherently an approximate theory [19, 14, 10]. The alternative approach is more recent. The use of nonequilibrium Green functions (NEGF) in tunneling theory was initiated by Caroli *et al.* and Feuchtwang [13, 14, 15, 16]. The theory is formally exact, it can handle electron-electron and electron-phonon interactions, and it generalizes the Landauer formula [17]. Two decades after the NEGF approach to tunneling was introduced, it was announced that Bardeen’s current formula can be understood as an approximation to the NEGF current formula “when an interface between tip and surface can be found on which the density of states is small” [18]. Whether you take the traditional or the NEGF approach, it requires extra effort to understand Bardeen’s theory.

In this article we expound Duke’s approach to Bardeen’s tunneling theory, discussing severally the contributions of Oppenheimer, Bardeen, Tersoff and Hamann, and Chen. Sections 2.1 and 2.2 explain Oppenheimer’s perturbation theory, and Section 2.3 exhibits Bardeen’s formulas for Oppenheimer’s matrix elements. Section 3 gives a version of C. J. Chen’s proof of the Tersoff-Hamann formula for the tunneling current. The final section discusses the application of Bardeen’s theory to scanning microscopy and spectroscopy in practice. We treat only Bardeen’s theory here; for comprehensive reviews of theories of scanning tunneling microscopy we refer the reader to [11, 12, 10].

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<sup>1</sup>Many books and papers on scanning tunneling microscopy simply cite Bardeen’s tunneling formula without explaining its provenance at all. Several sources do remark in passing that Bardeen’s current formula results from first-order perturbation theory, but this could mislead a casual reader into supposing that the formula can be derived by standard arguments.

## 2 Bardeen’s tunneling theory

Bardeen viewed the tunneling current as the net effect of many independent scattering events that transfer electrons across the tunneling barrier. With adequate knowledge of the electronic states of the sample and the tip, one can approximate the rates of these individual scattering events, and arrive at an expression for the tunneling current: it equals the net rate of transfer of electrons between tip and sample multiplied by the charge  $e$  of an electron. Bardeen’s tunneling theory (upon Duke’s interpretation) is based on several assumptions. Two of these assumptions are inherited from Oppenheimer’s “perturbation” theory:

- (O1) *tunneling is weak enough that the first-order approximation in Section 2.1 is valid;*
- (O2) *tip and sample states are nearly orthogonal.*

A few further assumptions belong to Bardeen’s theory itself:

- (B1) *the electron-electron interaction can be ignored;*
- (B2) *occupation probabilities for the tip and sample are independent of each other, and do not change, despite the tunneling;*
- (B3) *the tip and sample are each in electrochemical equilibrium.*

Neglecting the electron-electron interaction allows us to suppose that the electrons are independently governed by the single-electron Hamiltonian

$$H\psi = -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}). \quad (1)$$

$V(\mathbf{r})$  represents the electrostatic potential energy that an electron would have at position  $\mathbf{r}$  inside the STM. Assuming independent electrons, the problem of electronic dynamics in the STM devolves to the analysis of the single-electron Hamiltonian. One may reasonably disregard the electron-electron interaction in many STM experiments, but certainly not in every situation of interest. In particular, samples that exhibit single-electron charging effects cannot be treated by Bardeen’s theory because of Assumption B1 (see, e.g., [21, 22]).

Unfortunately, even the single-electron problem can be very difficult to solve: it is too hard to compute the eigenvalues and eigenfunctions of a Hamiltonian (1) in general. Bardeen’s idea was to leverage the knowledge we might have of the electronic structure of the tip and sample separately, considering them in isolation rather than as parts of the STM, in order to estimate the current through the tip-sample junction. To this end, Bardeen <sup>2</sup> defined tip and sample Hamiltonians

$$H_{sam}\psi = -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r}) + V_{sam}(\mathbf{r})\psi(\mathbf{r}) . \quad (2)$$

$$H_{tip}\psi = -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r}) + V_{tip}(\mathbf{r})\psi(\mathbf{r}) \quad (3)$$

in terms of tip and sample potentials  $V_{sam}$  and  $V_{tip}$  defined as follows. The space containing the STM is divided into three regions: the barrier region, the sample region, and the tip region. Bardeen set the sample potential  $V_{sam}(\mathbf{r})$  equal to  $V(\mathbf{r})$  for  $\mathbf{r}$  inside the sample and barrier regions, and equal to 0 for  $\mathbf{r}$  in the tip region; and he set  $V_{tip}(\mathbf{r}) = V(\mathbf{r})$  for  $\mathbf{r}$  inside the tip and barrier regions, but  $V_{tip}(\mathbf{r}) = 0$  for  $\mathbf{r}$  in the sample region. The boundaries between the barrier region and the tip and sample regions are drawn arbitrarily, and it is sometimes more convenient not to have a barrier region as such, but to divide the whole space between the tip and sample regions, giving some (or none, or all) of the barrier region to the tip region and the rest to the sample region.

The eigenfunctions of the tip and sample Hamiltonians (3) and (2) are called “tip states” and “sample states” respectively. The tunneling current is the result of the transfer of electrons from tip states to sample states (or vice versa) under the influence of the Hamiltonian (1) for the whole STM. To compute the current, one needs to know which tip and sample states are occupied by electrons. Assumptions B2 and B3 are required for this purpose. These are reasonable assumptions if the tip and sample are considered to be very large systems, each incorporating its own electron reservoir of virtually unlimited capacity, for then the tunneling of electrons will scarcely diminish or augment the density of states for the sample or tip.

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<sup>2</sup>Of course, Bardeen did not have the STM in mind when he wrote his tunneling theory, twenty years before the invention of the STM.

## 2.1 Single-electron scattering rates, after Oppenheimer

Consider an electron initially in the sample state  $\psi$  with energy  $\mathcal{E}$ , i.e.,  $H_{sam}\psi = \mathcal{E}\psi$ . Its wavefunction evolves into  $\psi(t)$  at time  $t$  from  $\psi$  at  $t = 0$ . If the evolution were governed by the sample Hamiltonian (2) alone, then  $\psi(t)$  would equal  $e^{-it\mathcal{E}/\hbar}\psi$ . Therefore, if the tunneling is weak, we anticipate that  $\psi(t)$  will be close to  $e^{-it\mathcal{E}/\hbar}\psi$  when  $t$  is small enough. So we write

$$\psi(t) = e^{-it\mathcal{E}/\hbar}\psi + \sum_k a_k(t)\phi_k, \quad (4)$$

where the sum is over all bound<sup>3</sup> states  $\phi_k$  of the tip Hamiltonian with  $H_{tip}\phi_k = E_k\phi_k$ . The goal is to approximate the coefficients  $a_k(t)$ . We know that  $a_k(0) = 0$  for all  $k$ , and Assumption O1 permits us to approximate  $a_k(t)$  for  $t > 0$  by a sort of perturbation theoretic calculation:

We plug (4) into the time-dependent Schrödinger equation for the STM to learn something about the  $a_k(t)$ 's. On the one hand, the time-dependent Schrödinger equation for the STM becomes

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r}, t) &= H\psi(\mathbf{r}, t) = H(e^{-it\mathcal{E}/\hbar}\psi) + \sum_k a_k(t)H\phi_k \\ &= e^{-it\mathcal{E}/\hbar}(H_{sam} + (H - H_{sam}))\psi + \sum_k a_k(t)(H_{tip} + (H - H_{tip}))\phi_k \\ &= e^{-it\mathcal{E}/\hbar}\mathcal{E}\psi + e^{-it\mathcal{E}/\hbar}(H - H_{sam})\psi + \sum_k a_k(t)(E_k\phi_k + (H - H_{tip})\phi_k). \end{aligned}$$

On the other hand, taking the time-derivative of  $\psi(t)$  in (4) leads to

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \mathcal{E}e^{-it\mathcal{E}/\hbar}\psi + i\hbar\sum_k \frac{d}{dt}a_k(t)\phi_k.$$

Putting the two hands together we get

$$i\hbar\sum_k \frac{d}{dt}a_k(t)\phi_k = e^{-it\mathcal{E}/\hbar}(H - H_{sam})\psi + \sum_k a_k(t)(E_k\phi_k + (H - H_{tip})\phi_k)$$

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<sup>3</sup>The coefficients in this expansion are  $a_k(t) = \langle \phi_k | \psi(t) - e^{-it\mathcal{E}/\hbar}\psi \rangle$ , so that  $\sum a_k(t)\phi_k$  is the projection of  $\psi(t) - e^{-it\mathcal{E}/\hbar}\psi$  onto the space spanned by the bound states of the tip. Since the tip's bound states do not span the whole space, Equation (4) is only approximate.

after we cancel the  $\mathcal{E}e^{-it\mathcal{E}/\hbar}\psi$  term. Taking the inner product of both sides of the preceding equation with  $\phi_j$  yields

$$i\hbar\frac{d}{dt}a_j(t) = e^{-it\mathcal{E}/\hbar}\langle\phi_j|H - H_{sam}|\psi\rangle + E_j a_j(t) + \sum_k a_k(t)\langle\phi_j|H - H_{tip}|\phi_k\rangle. \quad (5)$$

Equation (5) could be solved for  $a_j(t)$ , were it not for the terms  $a_k(t)\langle\phi_j|H - H_{tip}|\phi_k\rangle$  on the right-hand side. It is here we invoke Assumption O1 and assume that all of the  $a_k(t)$ 's, which are 0 to begin with, remain very small for a little while.<sup>4</sup> Then, as long as the coefficients remain small,  $a_j(t)$  should approximately satisfy the differential equation<sup>5</sup>

$$i\hbar\frac{d}{dt}a_j(t) = e^{-it\mathcal{E}/\hbar}\langle\phi_j|H - H_{sam}|\psi\rangle + E_j a_j(t). \quad (6)$$

The solution of (6) for the initial condition  $a_j(0) = 0$  is

$$a_j(t) = \frac{e^{-it\mathcal{E}/\hbar} - e^{-itE_j/\hbar}}{\mathcal{E} - E_j}\langle\phi_j|H - H_{sam}|\psi\rangle.$$

and therefore

$$|a_j(t)|^2 = \frac{4\sin^2(t(E_j - \mathcal{E})/2\hbar)}{(E_j - \mathcal{E})^2} \left| \langle\phi_j|H - H_{sam}|\psi\rangle \right|^2. \quad (7)$$

Assumption O2 is now required to relate the quantities  $|a_j(t)|^2$  to the transition probabilities  $|\langle\phi_j|\psi(t)\rangle|^2$ . From (4) we see that

$$\langle\phi_j|\psi(t)\rangle = a_j(t) + \langle\phi_j|\psi\rangle e^{-it\mathcal{E}/\hbar}.$$

If  $\langle\phi_j|\psi\rangle$  is small relative to  $a_j(t)$ , then  $|a_j(t)|^2$  is the main part of the transition probability  $|\langle\phi_j|\psi(t)\rangle|^2$ , and  $\frac{d}{dt}\sum_j |a_j(t)|^2$  then approximates the rate at which an electron initially in the sample state  $\psi$  “scatters into” a tip state under the influence of the STM Hamiltonian (1). The assumption that the inner products  $\langle\phi_j|\psi\rangle$  be very small is quite explicit in [20].

Assuming O1 and O2, the total rate at which an electron initially in the sample state  $\psi$

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<sup>4</sup>We will find that it is sufficient for the following approximation to hold up to a few picoseconds.

<sup>5</sup>We have kept the term  $E_j a_j(t)$  even though we are assuming that the  $a_k(t)$ 's are small, because we can solve the differential equation without neglecting it, and get a better approximation for  $a_j(t)$  at the end.

scatters into tip states is approximately

$$\frac{d}{dt} \sum_k |a_k(t)|^2 = \frac{d}{dt} 4 \sum_k \frac{\sin^2(t(E_k - \mathcal{E})/2\hbar)}{(E_k - \mathcal{E})^2} \left| \langle \phi_k | H - H_{sam} | \psi \rangle \right|^2. \quad (8)$$

Formula (8) is also the total rate that electrons in tip states scatter into a given sample state  $\psi$ . (This dual interpretation of formula (8) is due to the formal symmetry between sample and tip in the preceding arguments.) If one knows which sample and tip states are occupied by electrons, a formula for the current can be assembled from the scattering rate formulas (8).

Assumption O2, that tip and sample states are nearly orthogonal, is essential to Oppenheimer’s perturbation theory: it allows one to approximate the transition probability  $|\langle \phi_j | \psi(t) \rangle|^2$  by  $|a_j(t)|^2$ . Because of this, Oppenheimer’s perturbation theory is inherently approximate, in the sense that formula (8) would still be only an approximate expression for the total scattering rate even if equation (5) could be solved *exactly*. The estimate (7) of  $|a_j(t)|^2$  could perhaps be improved by a higher-order treatment of (5), but  $\frac{d}{dt}|a_j(t)|^2$  would still only approximate the meaning we assign to it, namely, the rate at which an electron that starts in the sample state  $\psi$  “scatters into” the tip state  $\phi_j$ .

## 2.2 Total scattering rate, after Fermi

The sum in (8) can be approximated by Fermi’s Golden Rule since there are very many tip states [23]. Fermi’s Golden Rule is only valid at times  $t$  which are large enough that the density of (tip) states per unit energy is nearly constant on the energy scale  $h/t$ , where  $h$  is Planck’s constant [24, 25]. Each STM tip is different,<sup>6</sup> but its density of states will be nearly constant on intervals of 10meV, and therefore the formulas obtained from (8) by Fermi’s Golden Rule will be valid when  $t$  is a picosecond or so. Since formula (8) itself is only valid for as long as solutions of (6) are good approximations of solutions of (5), Assumption O1 must guarantee that Oppenheimer’s first-order approximation works at least up to picoseconds.

The idea of Fermi’s Golden Rule is to approximate the sum in (8) by an integral with respect

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<sup>6</sup>See Ref.s [26, 27, 28] for experimental and theoretical studies of tip spectra.

to energy. The sum on the right-hand side of (8) can be written as

$$\sum_k P_t(E_k - \mathcal{E}) \mathcal{M}^2(\phi_k, \psi) , \quad (9)$$

where  $\mathcal{M}^2(\phi, \psi) = |\langle \phi | H - H_{sam} | \psi \rangle|^2$  and  $P_t(x) = \sin^2(tx/2\hbar)/x^2$ . The function  $P_t(x)$  is nonnegative and its integral with respect to  $x$  equals  $\pi t/2\hbar$ , but the main contribution to this integral comes from the interval  $-2\hbar/t < x < 2\hbar/t$ . When  $t$  is large enough, the energy interval  $-2\hbar/t < E < 2\hbar/t$  becomes so narrow that the tip energy levels  $E_k$  appear to be distributed with constant density over that energy interval. Let  $\rho_{tip}(\mathcal{E})$  denote this ‘‘density of states’’ at  $\mathcal{E}$ , that is, the number of tip states per unit energy near  $\mathcal{E}$ . Letting  $N_{\mathcal{E}}$  denote the number of tip states with energies in the energy interval  $-2\hbar/t + \mathcal{E} < \varepsilon < 2\hbar/t + \mathcal{E}$ , and setting

$$\mathcal{M}^2(\psi) = \frac{1}{N_{\mathcal{E}}} \sum_{k: |E_k - \mathcal{E}| < 2\hbar/t} \mathcal{M}^2(\phi_k, \psi) , \quad (10)$$

we can approximate (9) as follows:<sup>7</sup>

$$\sum_k P_t(E_k - \mathcal{E}) \mathcal{M}^2(\phi_k, \psi) \approx \sum_{k: |E_k - \mathcal{E}| < \frac{2\hbar}{t}} P_t(E_k - \mathcal{E}) \mathcal{M}^2(\phi_k, \psi) \quad (11)$$

$$\approx \mathcal{M}^2(\psi) \sum_{k: |E_k - \mathcal{E}| < 2\hbar/t} P_t(E_k - \mathcal{E}) \quad (12)$$

$$\approx \mathcal{M}^2(\psi) \rho_{tip}(\mathcal{E}) \int_{-2\hbar/t}^{2\hbar/t} P_t(E) dE \approx \mathcal{M}^2(\psi) \rho_{tip}(\mathcal{E}) \int_{-\infty}^{\infty} P_t(E) dE$$

$$= \mathcal{M}^2(\psi) \rho_{tip}(\mathcal{E}) \frac{\pi t}{2\hbar} .$$

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<sup>7</sup>Approximation (12) involves an additional assumption that  $P_t(E_k - \mathcal{E})$  and  $\mathcal{M}^2(\phi_k, \psi)$  are statistically uncorrelated for the ‘‘population’’ consisting of tip states  $\phi_k$  belonging to the energy interval. To see this, multiply the the sum on the right-hand side of (11) by  $1/N_{\mathcal{E}}$  and think of that quantity as the average of  $P_t(E_k - \mathcal{E}) \mathcal{M}^2(\phi_k, \psi)$  over all tip states in the energy interval. If  $P_t(E_k - \mathcal{E})$  and  $\mathcal{M}^2(\phi_k, \psi)$  are uncorrelated, then the average of their product equals the product of their averages. The average of the  $\mathcal{M}^2(\phi_k, \psi)$  is  $\mathcal{M}^2(\psi)$  as defined in (10) and the average of the  $P_t(E_k - \mathcal{E})$  equals  $1/N_{\mathcal{E}}$  times the sum in (12).

Substituting the latter expression for the sum on the right-hand side of (8), we find that

$$\frac{d}{dt} \sum_k |a_k(t)|^2 \approx \frac{d}{dt} \left( \frac{2\pi t}{\hbar} \mathcal{M}^2(\psi) \rho_{tip}(\mathcal{E}) \right) = \frac{2\pi}{\hbar} \mathcal{M}^2(\psi) \rho_{tip}(\mathcal{E}) . \quad (13)$$

Formula (13) would be the rate at which electrons in the sample state  $\psi$  are transferred into tip states of comparable energy if all of those states were *vacant* and available to receive electrons. However, Pauli's Exclusion Principle declares that at most one electron may occupy a given tip state, so the density of states  $\rho_{tip}(\mathcal{E})$  in (13) needs to be multiplied by the fraction of unoccupied tip states with energies near  $\mathcal{E}$ . Assuming (B2 and B3) that the occupation statistics of the tip are constantly those of Fermi-Dirac equilibrium at temperature  $\theta$  and chemical potential  $\mu_t$ , the rate of scattering from  $\psi$  into a tip state becomes

$$(1 - F_{\mu_t, \theta}(\mathcal{E})) \frac{2\pi}{\hbar} \rho_{tip}(\mathcal{E}) \mathcal{M}^2(\psi) , \quad (14)$$

where

$$F_{\mu, \theta}(x) = \frac{1}{e^{(x-\mu)/k_B\theta} + 1} \quad (15)$$

is the Fermi-Dirac function for temperature  $\theta$  and chemical potential  $\mu$  (and  $k_B$  is Boltzmann's constant). Similarly, formula (13) would be the rate at which electrons move from all tip states of energy near  $\mathcal{E}$  into the sample state  $\psi$  if all of those tip states were *occupied* by electrons. But only a fraction of these tip states are occupied. Again, assuming that the occupation probabilities of tip states are always given by  $F_{\mu_t, \theta}$ , the rate at which an electron in some tip state transports itself into the sample state  $\psi$  is

$$F_{\mu_t, \theta}(\mathcal{E}) \frac{2\pi}{\hbar} \rho_{tip}(\mathcal{E}) \mathcal{M}^2(\psi) . \quad (16)$$

Formula (14) tells us the total rate of scattering into tip states from an individual sample state  $\psi_n$  with energy  $\mathcal{E}_n$ , and formula (16) tells us the total rate of scattering into that sample state from all tip states. To find the net current, we need to know which sample states are occupied and which are vacant. Occupied sample states contribute a current of electrons from the sample to tip at rate (14), and vacant sample states enable electrons to flow from the tip to the sample at rate (16). Assuming (B2 and B3) that the occupation probabilities of the

sample states are always those of equilibrium at temperature  $\theta$  and chemical potential  $\mu_s$ , the probability that there is an electron in the sample state  $\psi_n$  with  $H_{sam}\psi_n = \mathcal{E}_n\psi_n$  is  $F_{\mu_s,\theta}(\mathcal{E}_n)$ , the Fermi-Dirac function (15) for temperature  $\theta$  and chemical potential  $\mu_s$ . Summing over the sample states weighted by their occupation probabilities, we get a formula for the total rate at which sample electrons scatter into tip electrons and vice versa; multiplying the difference of these two rates by the electronic charge  $e$  we get a formula for the tunneling current  $I$  from sample to tip. That is, the electronic current is  $e$  times the sum over sample states  $\psi_n$  of the difference between (i) the probability that the sample state  $\psi_n$  is vacant times the rate (16) of electron transfer from some tip state into  $\psi_n$ , and (ii) the probability that the sample state  $\psi_n$  is occupied times the rate (14) of electron transfer from  $\psi_n$  into the tip:

$$I = \frac{2\pi e}{\hbar} \sum_n \{F_{\mu_t,\theta}(\mathcal{E}_n)(1 - F_{\mu_s,\theta}(\mathcal{E}_n)) - (1 - F_{\mu_t,\theta}(\mathcal{E}_n))F_{\mu_s,\theta}(\mathcal{E}_n)\} \rho_{tip}(\mathcal{E}_n) \mathcal{M}^2(\psi_n) . \quad (17)$$

**Formula for current at low temperature:** At  $\theta = 0$ , the Fermi-Dirac function  $F_{\mu,\theta}(x)$  of formula (15) degenerates into a Heaviside function, i.e.,  $F_{\mu,0}(x) = 1$  if  $x < \mu$  and  $F_{\mu,0}(x) = 0$  if  $\mu < x$ , and the tunneling current formula (17) becomes

$$I = \pm \frac{2\pi e}{\hbar} \sum_{n: \mu_a < \mathcal{E}_n < \mu_b} \rho_{tip}(\mathcal{E}_n) \mathcal{M}^2(\psi_n) , \quad (18)$$

where  $\mu_a = \min\{\mu_s, \mu_t\}$ ,  $\mu_b = \max\{\mu_s, \mu_t\}$ , and the sign is  $+$  or  $-$  depending on whether  $\mu_t > \mu_s$  or  $\mu_t < \mu_s$ , respectively. The sum in (18) can be approximated by an integral:

$$I = \pm \frac{2\pi e}{\hbar} \int_{\mu_a}^{\mu_b} \rho_{tip}(\varepsilon) T(\varepsilon) \rho_{sam}(\varepsilon) d\varepsilon , \quad (19)$$

where  $T(\varepsilon)$  is the average value of  $\mathcal{M}^2(\psi_n)$  over all sample states  $\psi_n$  whose energy  $\mathcal{E}_n$  lies in a small interval centered at  $\varepsilon$ .<sup>8</sup> Note that  $\rho_{tip}$ ,  $\rho_{sam}$ , and  $T(\varepsilon)$  in formula (19) all depend on  $\mu_t$  and  $\mu_s$ , because maintaining a bias across the tunneling junction distorts the shape of the potential  $V(\mathbf{r})$  in and near the barrier (this phenomenon is known as “band bending”).

**Formula for current at low temperature and low bias:** Formula (19) for the current

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<sup>8</sup>The energy interval used to define  $T(\varepsilon)$  must be wide enough to include the energy levels of many sample states, yet narrow enough that these energy levels are apportioned evenly over the width of the interval.

at 0 Kelvin can be further simplified if the bias is low enough. When  $\mu_s$  and  $\mu_t$  are so close that the  $\rho_{sam}(\varepsilon)$  and  $\rho_{tip}(\varepsilon)$  are each nearly constant over the energy interval  $\mu_a < \varepsilon < \mu_b$ , formula (19) reduces to

$$I = \pm \frac{2\pi e}{\hbar} (\mu_b - \mu_a) \rho_{tip}(\mu) \rho_{sam}(\mu) T(\mu), \quad (20)$$

where  $\mu$  is any number in between  $\mu_a$  and  $\mu_b$ . Also, since the density of sample states over the energy interval  $\mu_a < \varepsilon < \mu_b$  is constant, the number of sample states with energies between  $\mu_a$  and  $\mu_b$  is  $(\mu_b - \mu_a) \rho_{sam}(\mu)$ , and therefore

$$T(\mu) = \frac{1}{(\mu_b - \mu_a) \rho_{sam}(\mu)} \sum_{\psi_n: \mu_a < \mathcal{E}_n < \mu_b} \mathcal{M}^2(\psi_n) \quad (21)$$

by definition. Substituting (21) into formula (20) brings us to the following formula for the tunneling current at low temperature and low bias:

$$I = \pm \frac{2\pi e}{\hbar} \rho_{tip}(\mu) \sum_{\psi_n: \mu_a < \mathcal{E}_n < \mu_b} \mathcal{M}^2(\psi_n) \quad (22)$$

(recall that  $\mu_a = \min\{\mu_s, \mu_t\}$ ,  $\mu_b = \max\{\mu_s, \mu_t\}$ , and  $\mu$  is any number between  $\mu_a$  and  $\mu_b$ ).

### 2.3 Approximating the matrix elements, after Bardeen

Now we have formulas for current that depend on the matrix elements

$$\langle \phi_j | H - H_{sam} | \psi_n \rangle = \int (V(\mathbf{r}) - V_{sam}(\mathbf{r})) \overline{\phi_j(\mathbf{r})} \psi_n(\mathbf{r}) d\mathbf{r}. \quad (23)$$

Bardeen found a more symmetric expression for these matrix elements (formula (26) below) and showed that the volume integral in (23) can be approximated by a flux through a “separation surface” in the barrier region.

Choose any smooth surface in the barrier region that separates the tip and sample. Let  $\partial T$  denote this separation surface and let  $T$  denote the region consisting of all points on the same side of  $\partial T$  as the tip. The operator  $H - H_{tip}$  is the zero operator on the tip side of the

separation surface, and therefore

$$\begin{aligned}
0 &= \int_T \psi_n(\mathbf{r})(H - H_{tip})\overline{\phi_j(\mathbf{r})}d\mathbf{r} = \int_T \psi_n(\mathbf{r})H\overline{\phi_j(\mathbf{r})}d\mathbf{r} - E_j \int_T \psi_n(\mathbf{r})\overline{\phi_j(\mathbf{r})}d\mathbf{r} \\
&= -\frac{\hbar^2}{2m} \int_T \psi_n(\mathbf{r})\Delta\overline{\phi_j(\mathbf{r})}d\mathbf{r} + \int_T \psi_n(\mathbf{r})V(\mathbf{r})\overline{\phi_j(\mathbf{r})}d\mathbf{r} - E_j \int_T \psi_n(\mathbf{r})\overline{\phi_j(\mathbf{r})}d\mathbf{r}. \quad (24)
\end{aligned}$$

On the other hand, since  $H - H_{sam}$  is the zero operator on the sample side of the surface, the matrix element (23) can be written as an integral over  $T$ :

$$\begin{aligned}
\langle \phi_j | H - H_{sam} | \psi_n \rangle &= \int_T \overline{\phi_j(\mathbf{r})}(H - H_{sam})\psi_n(\mathbf{r})d\mathbf{r} = \int_T \overline{\phi_j(\mathbf{r})}H\psi_n(\mathbf{r})d\mathbf{r} - \mathcal{E}_n \int_T \overline{\phi_j(\mathbf{r})}\psi_n(\mathbf{r})d\mathbf{r} \\
&= -\frac{\hbar^2}{2m} \int_T \overline{\phi_j(\mathbf{r})}\Delta\psi_n(\mathbf{r})d\mathbf{r} + \int_T \overline{\phi_j(\mathbf{r})}V(\mathbf{r})\psi_n(\mathbf{r})d\mathbf{r} - \mathcal{E}_n \int_T \overline{\phi_j(\mathbf{r})}\psi_n(\mathbf{r})d\mathbf{r}. \quad (25)
\end{aligned}$$

Subtracting (24) from (25), we find that

$$\begin{aligned}
\langle \phi_j | H - H_{sam} | \psi_n \rangle &= \int_T \overline{\phi_j(\mathbf{r})} \left( -\frac{\hbar^2}{2m} \Delta\psi_n(\mathbf{r}) - \mathcal{E}_n \psi_n(\mathbf{r}) \right) d\mathbf{r} \\
&\quad - \int_T \psi_n(\mathbf{r}) \left( -\frac{\hbar^2}{2m} \Delta\overline{\phi_j(\mathbf{r})} - E_j \overline{\phi_j(\mathbf{r})} \right) d\mathbf{r} \quad (26)
\end{aligned}$$

To obtain the tunneling current by Fermi's Golden Rule we only consider matrix elements for which  $\mathcal{E}_n$  and  $E_j$  are approximately equal (within a few meV of one another). Assuming  $\mathcal{E}_n \approx E_j$ , formula (26) for the matrix elements tells us that

$$\begin{aligned}
\langle \phi_j | H - H_{sam} | \psi_n \rangle &\approx -\frac{\hbar^2}{2m} \int_T \left[ \overline{\phi_j(\mathbf{r})}\Delta\psi_n(\mathbf{r}) - \psi_n(\mathbf{r})\Delta\overline{\phi_j(\mathbf{r})} \right] d\mathbf{r} \\
&= -\frac{\hbar^2}{2m} \int_T \nabla \cdot \left[ \overline{\phi_j(\mathbf{r})}\nabla\psi_n(\mathbf{r}) - \psi_n(\mathbf{r})\nabla\overline{\phi_j(\mathbf{r})} \right] d\mathbf{r} \quad (27)
\end{aligned}$$

up to an error of magnitude  $|\mathcal{E}_n - E_j|$ . The right-hand side of (27) can be written as a surface (flux) integral by the Divergence Theorem of vector calculus:

$$\int_T \nabla \cdot \left[ \overline{\phi_j(\mathbf{r})}\nabla\psi_n(\mathbf{r}) - \psi_n(\mathbf{r})\nabla\overline{\phi_j(\mathbf{r})} \right] d\mathbf{r} = \int_{\partial T} \left[ \overline{\psi_n(\mathbf{r})}\nabla\phi_j(\mathbf{r}) - \phi_j(\mathbf{r})\nabla\overline{\psi_n(\mathbf{r})} \right] \cdot d\mathbf{n}$$

where  $\mathbf{n}$  denotes the normal vector to the surface  $\partial T$ , oriented outward from  $T$ . This results in Bardeen's approximation of the matrix element:

$$\langle \phi_j | H - H_{sam} | \psi_n \rangle \approx -\frac{\hbar^2}{2m} \int_{\partial T} \left[ \overline{\psi_n(\mathbf{r})} \nabla \phi_j(\mathbf{r}) - \phi_j(\mathbf{r}) \nabla \overline{\psi_n(\mathbf{r})} \right] \cdot d\mathbf{n} . \quad (28)$$

### 3 The Tersoff-Hamann formula

In 1983, Tersoff and Hamann [8] applied Bardeen's formula (28) to the STM. Modeling the electronic wavefunctions of the tip by radially symmetric wavefunctions, Tersoff and Hamann deduced a useful rule-of-thumb: the tunneling current is proportional to the part of the electronic density at the center of the tip due to the sample wavefunctions at the quasi-Fermi energy  $\mu$ .

A much better proof of the Tersoff-Hamann formula was later found by C.J. Chen [29]. The Tersoff-Hamann formula is obtained if the tip states can be modeled by the spherically symmetric form  $\phi_j(\mathbf{r}) \approx A_j e^{-\kappa_j r} / r$  outside the tip region, where  $r$  is the distance to the center of the tip, which we imagine to be located at the origin  $\mathbf{0} = (0, 0, 0)$  for convenience, and  $A_j$  is a constant. If the tip potential  $V_{tip}(\mathbf{r})$  were a radially symmetric potential well with  $V_{tip}(\mathbf{r}) = 0$  for  $|\mathbf{r}| \equiv r > R$ , this is the form that the radial part of any tip state would take where  $r \gg R$ . The decay constant  $\kappa_j$  must equal  $\sqrt{2m|E_j|}/\hbar$ , so that

$$\Phi_j(\mathbf{r}) = e^{-\kappa_j r} / r \quad (29)$$

can satisfy the vacuum Schrödinger equation

$$-\frac{\hbar^2}{2m} \Delta(e^{-\kappa_j r} / r) = E_j e^{-\kappa_j r} / r$$

when  $r > R$ , at points outside of the tip region. C.J. Chen's insight is that  $\Phi_j(\mathbf{r})$  satisfies the following equation at all points

$$-\frac{\hbar^2}{2m} \Delta \Phi_j(\mathbf{r}) - E_j \Phi_j(\mathbf{r}) = \frac{\hbar^2}{2m} 4\pi \delta_0(\mathbf{r}) \quad (30)$$

in the sense of “distributions,” i.e., when  $\Phi_j$  identifies a generalized function like the Dirac delta distribution appearing on the right-hand side of (30). Let us approximate  $\phi_j(\mathbf{r})$  by  $A_j\Phi_j(\mathbf{r})$  in the sample region. The constant  $A_j$  is not fixed by the normalization condition on  $\phi_j$ , for  $\phi_j(\mathbf{r})$  only takes the form  $A_j\Phi_j(\mathbf{r})$  *outside* of the tip region; rather,  $A_j$  depends on the effective radius  $R$  of the tip and other considerations.

Using formula (26) to calculate the matrix element  $\langle\Phi_j|H - H_{sam}|\psi_n\rangle$ , let us choose  $T$  to be the tip region itself, not including any of the barrier region at all. Since all sample states  $\psi_n$  satisfy  $-\frac{\hbar^2}{2m}\Delta\psi_n = \mathcal{E}_n\psi_n$  in the tip region, while  $e^{-\kappa_j r}/r$  satisfies (30) in the tip region, we find that

$$\begin{aligned}\langle\phi_j|H - H_{sam}|\psi_n\rangle &\approx \langle A_j\Phi_j|H - H_{sam}|\psi_n\rangle \\ &= -\overline{A_j} \int_T \psi_n(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\Delta\Phi_j(\mathbf{r}) - E_j\Phi_j(\mathbf{r})\right) d\mathbf{r} \\ &= -\overline{A_j} \int_T \psi_n(\mathbf{r}) \frac{\hbar^2}{2m} 4\pi\delta_0(\mathbf{r}) d\mathbf{r} \\ &= -\frac{\hbar^2}{m} 2\pi\overline{A_j}\psi_n(\mathbf{0}).\end{aligned}\tag{31}$$

Thus the squared matrix element  $\mathcal{M}^2(\phi_j, \psi_n)$  is approximated by  $(\frac{\hbar^2}{m}2\pi)^2|A_j|^2|\psi_n(\mathbf{0})|^2$ . By (10),

$$\mathcal{M}^2(\psi_n) = (\frac{\hbar^2}{m}2\pi)^2 A^2 |\psi_n(\mathbf{0})|^2,$$

where  $A^2$  is the average of  $|A_j|^2$  over all  $j$  such that  $\phi_j$  is a tip state in a small energy interval about  $\mathcal{E}_n$ .

For low bias across the tunneling junction, we obtain the following Tersoff-Hamann formula<sup>9</sup> for the current from (22):

$$\begin{aligned}I &= \pm \frac{2\pi e}{\hbar} \rho_{tip}(\mu) \left(\frac{\hbar^2}{m}2\pi\right)^2 A^2 \sum_{\psi_n: \mu_a < \mathcal{E}_n < \mu_b} |\psi_n(\mathbf{0})|^2 \\ &= (\mu_t - \mu_s) \frac{e\hbar^3}{m^2} A^2 \rho_{tip}(\mu) \rho_s(\mathbf{0}, \mu),\end{aligned}\tag{32}$$

---

<sup>9</sup>This formula is equivalent to formula (9) of [8] or [30] when  $A = Re^{\kappa R}/(\frac{4}{3}\pi R^3)^{1/2}$ , where  $R$  is the effective radius of the tip.

where

$$\rho_s(\mathbf{r}, \mu) = \frac{1}{|\mu_s - \mu_t|} \sum_{\psi_n: \mu_a < \mathcal{E}_n < \mu_b} |\psi_n(\mathbf{r})|^2$$

is the “local density of sample states” per unit volume near the point  $\mathbf{r}$  and per unit energy near the quasi-Fermi energy  $\mu$ . Thus, the Tersoff-Hamann formula predicts that the conductance of an STM at low temperature and low bias is proportional to the local density of sample states at the center of the tip and the quasi-Fermi energy.

## 4 Discussion

We have seen what assumptions underlie Bardeen’s current formula (17) and the Tersoff-Hamann formula (32). But when are these formulas supposed to be accurate, in practice, and are the assumptions really valid in those situations?

Tersoff and Hamann’s formula is only valid for low bias across the tunneling junction. The formula does not apply when the sample is a normally doped semiconductor surface, because a large bias (about 2V) is required to draw a tunneling current through the semiconductor [9]. Large biases are also routinely imposed when one does tunneling spectroscopy with an STM (to find the current-voltage characteristic when the tip is situated at a fixed point above the sample). Formula (19) of Bardeen’s theory does apply when there is a large bias across the barrier, but to use the formula properly it is necessary to understand how the tip and sample states change due to distortion of the potential profile by the bias. Nonetheless, formula (19) can provide valuable intuition for spectroscopy [31, 32, 33] and semiconductor imaging [34] with the STM.

One review of scanning probe microscopies [11] judges the Tersoff-Hamann model to be reliable for interpreting images of surface structures whose “feature size . . . is well above the typical length scale of electron states of the STM tip,” provided there are “no substantial chemical interactions between surface and tip.” Tersoff-Hamann theory is thus deemed adequate for images whose feature size is well above 1 or 2Å, when those images are produced at a large enough tip-sample distance (for metal surfaces, the tip-sample distance should be “larger than 5 – 6Å”).

Tersoff-Hamann theory is unable to account for atomic-resolution features of an STM image, but only because it ignores the detailed structure of the tip wavefunctions. Bardeen’s theory *without* the spherical tip approximation *can* account for atomic-resolution, provided the tip-sample distance is large enough that Assumptions O1 and O2 hold. C. J. Chen invented an ingenious extension of Tersoff-Hamann theory that accommodates more detailed models of the tip structure and allows one to interpret higher resolution features in STM images [35, 29, 36]. The idea is to model the tip wavefunction  $\phi_j(\mathbf{r})$  *outside of the tip region* as a linear combination of the wavefunction  $\Phi_j$  of formula (29) and its (first and higher) partial derivatives. Any partial derivative of  $\Phi_j$  satisfies the equation obtained by taking the same partial derivatives of both sides of equation (30), and therefore the matrix element (31) will involve partial derivatives of  $\psi(\mathbf{r})$  at  $\mathbf{0}$ . This is Chen’s “derivative rule” [29]. Alternatively, one may use formula (17) of Bardeen’s theory for the STM without modeling the tip after Tersoff-Hamann and Chen, when the electronic structure of the tip wavefunctions is known from another source (such as a density functional theoretic computation). This approach has been taken by several authors, using various tip models, from an atom adsorbed onto a jellium surface [37, 38], to little pyramids of tungsten atoms [39, 40], to tungsten surfaces with protruding atoms or clusters [41].

When the tip is close enough to the sample, chemical forces come into play, and the STM becomes unstable [42]. Once the tip gets *too* close — about  $4.1\text{\AA}$  from a metal surface according to one study [11, 43] — it will jump suddenly into contact with the sample. At higher tip-sample distances, up to about  $4.6$  or  $4.7\text{\AA}$ , there is still significant chemical interaction between the sample and tip. The main effect is to change the positions of tip and sample atoms [43]. Are Bardeen’s formulas of Section 2.3 still valid in this range of tip-sample distances? To compute the correct matrix elements at low tip-sample distances, one must know where the tip and sample atoms have been moved by the interaction, and one must take into account the actual electrostatic potential profile that results from those displacements. The tip or sample wavefunctions are not those of the isolated tip or sample; they are the eigenfunctions of the Hamiltonians (2) and (3), and these do not look quite like the states of the isolated separate tip or sample. If one is careful about this point then one may still use Bardeen’s formulas for the tunneling current, even within the range of chemical forces [1, 36]. This has been done in a study by Hofer *et al.* [44], who conclude that the images predicted by Bardeen’s theory are

in qualitative agreement with STM images of Fe(100) even when the tip-sample difference is as low as 4Å.

However, if the tip of an STM is mounted on a oscillating quartz force sensor used for atomic force microscopy [45], the tip can come very close to the surface before it rebounds away again, and higher resolution images can thus be attained without destroying the tip [46]. This kind of “dynamic STM” can even detect subatomic structure! A dynamic STM image generated by a samarium tip atom over a silicon surface in the presence of a magnetic field shows what appear to be lobes of a  $4f$  orbital, and looks like the image predicted by careful Bardeen-theoretic calculations [46].

But the success of Bardeen’s theory does not really prove that the underlying assumptions are valid. The most important of these is Assumption O1, concerning the accuracy of the first-order approximation. We have found that formula (8) must approximate the scattering rate accurately up to a few picoseconds, if we wish to apply Fermi’s Golden Rule as done in Section 2.2. The question is: how far away must the tip be from the sample for solutions of (6) to approximate solutions of (5) up to one picosecond or longer? The answer to this question would best indicate when Bardeen’s theory may be applied to the STM.

**Acknowledgments:** This work came about thanks to the conference “Mathematics of Nanoscale Science and Engineering” at the Institute for Pure and Applied Mathematics. This work was supported by the Austrian Ministry of Science (BM:BWK) via its grant for the Wolfgang Pauli Institute and by the Austrian Science Foundation (FWF) via the START Project (Y-137-TEC) of N. Mauser. A. G. thanks N. J. Mauser for his encouragement and involvement with this paper. L. W. thanks J. K. Gimzewski for his helpful suggestions, and we also thank him for permission to use the STM images presented in this paper.

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