

Application of the Friedel sum rule to symmetric molecular conductors

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Recent developments in nanotechnology have made it possible to measure the resistance of individual molecular wires self-assembled between two metallic pads. In this paper we present a simple expression for the resistance of a symmetric molecule in terms of a set of M phase shifts, M being the number of conducting channels connecting the molecule to the metallic pads. These phase-shifts are related by a sum rule to $N_d = N_{\text{even}} - N_{\text{odd}}$, where N_{even} and N_{odd} are the number of electrons occupying the even and odd eigenstates respectively. For many molecular wires of interest all the phase shifts are nearly zero except for one (per spin), allowing us to write a particularly simple relation for the resistance: $R^{-1} = (2e^2/h) \sin^2(\pi N_d/2)$. The relations presented here are based on the Friedel sum rule and should be valid even in the presence of interactions. [S0163-1829(97)50104-4]

A number of experimental groups have recently reported the observation of electronic conduction through "molecular wires" attached to two metallic contacts by special functional groups at the ends (Fig. 1).¹⁻⁷ Some of these molecular wires are based on alkane chains and are strongly insulating. Others are based on conjugated polymers like polyparaphenylene and could possibly be engineered to provide good electronic coupling, although so far the measured resistance has been at least several megohms per molecule. Theoretical work in this area has been based on the Landauer formula which relates the measured resistance R to the transmission function at the Fermi energy:⁸

$$R^{-1} = (e^2/h) T(E_f) = (25.8 \text{ k}\Omega)^{-1} T(E_f). \quad (1)$$

Different authors use different methods for calculating the transmission function but their results are similar and in general agreement with the available experimental data.⁹⁻¹¹ Note that the minimum possible resistance predicted by Eq. (1) is $(25.8/M)$ kilo-ohms corresponding to a "ballistic" molecule with $T(E_f) = M$, M being the number of conducting channels or transverse modes (including spin) that connect the molecule to the metallic pads at each end. This represents the contact resistance at the metal-molecule interface.

In this paper we will combine the Landauer formula with the Friedel sum rule¹²⁻¹⁵ to show that the resistance of any symmetric molecule can be written as

$$R^{-1} = \frac{e^2}{h} \sum_{m=1}^M \sin^2 \phi_m, \quad (2a)$$

where

$$\sum_{m=1}^M \phi_m = \pi(N_{\text{even}} - N_{\text{odd}}) \equiv \pi N_d, \quad (2b)$$

N_{even} and N_{odd} being the number of electrons occupying the even and odd states, respectively. The important point about Eq. (2) is that it should hold in general regardless of the detailed nature of the electron-electron interactions, although the function $N_d(E_f)$ or $T(E_f)$ might change drastically. This is because it is based on a general principle like the Friedel sum rule which has been shown to be valid for interacting systems assuming that the single-particle-like states do not decay.⁴ Consequently, we expect Eq. (2) to be accurate as

long as the broadening of the molecular levels due to the coupling to the leads is larger than any broadening due to interactions within the molecule. The generality of Eq. (2) could make it particularly useful in describing open shell molecules for which correlation effects can be quite complex. Also, the charge on a molecule (and hence the number of electrons) is experimentally observable so that it is more useful to know the transmission T as a function of the number of electrons rather than as a function of the Fermi energy E_f .

Equation (2) expresses the transmission in terms of the phase shifts ϕ_m in a manner reminiscent of the well-known expression for the scattering cross section (σ) of an impurity in a metal derived from the Friedel sum rule (here the transverse modes " m " are given by the spherical harmonics):

$$\sigma = \sum_{m=0}^{\infty} \sin^2 \delta_m,$$

where $\sum_{m=0}^{\infty} \delta_m = \pi N$.

This relation is particularly useful if one can guess the individual δ_m using general symmetry considerations. The same is true of Eq. (2). For example, for the molecule shown in Fig. 1(a), only two of the phase shifts are nonzero in the energy range around the HOMO-LUMO gap. For this molecule, we can identify the sulphur atoms at each end as the "leads," since electrons flow out into the reservoir from these sites. Since a sulphur atom has one s level and three p levels this means that, including spin, the molecule has eight modes in each lead: $M = 8$.¹⁶ But as we will see, of the eight distinct phase shifts ϕ_m , six are approximately zero. Noting that due to spin degeneracy the other two phase shifts are equal, it is easy to see that in this case we can write approximately from Eq. (2):

$$R^{-1} \approx (2e^2/h) \sin^2(\pi N_d/2). \quad (3)$$

The reason only one phase shift per spin is significant is that conduction takes place primarily through the p_z orbitals only so that the molecule effectively has only a single mode per spin. From this point of view, *the number of nonzero phase shifts is the real indicator of the number of modes* in a structure. The number of modes M in the leads is arbitrary, since

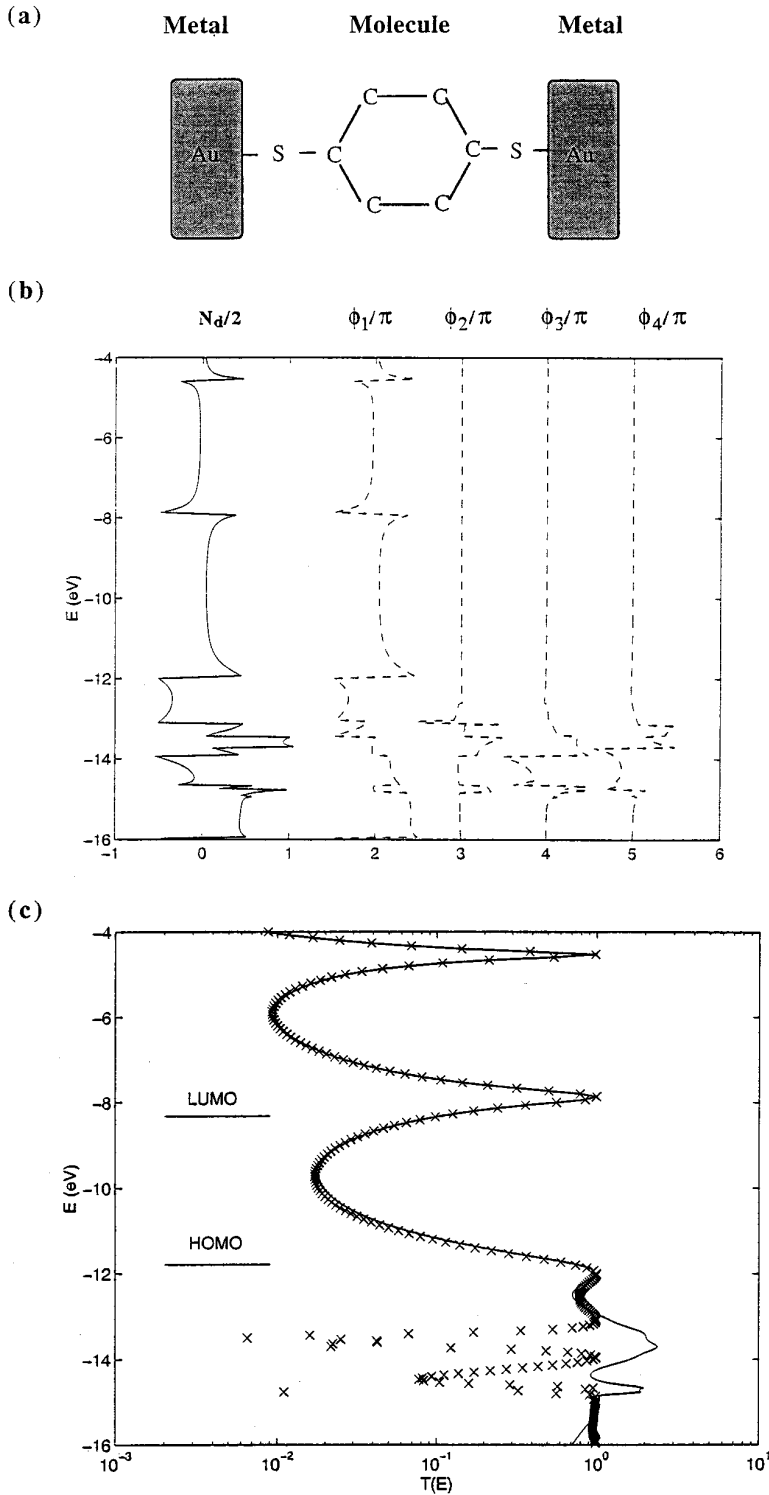


FIG. 1. (a) Chemical structure. (b) Phase shifts $\phi_m(E)$ ($m=1-4$) calculated from the eigenvalues of the $[r+t][r^+-t^+]$. Also shown is the function $\pi N_d = \pi(N_{\text{even}} - N_{\text{odd}})$ (divided by 2 for spin), which is equal to the sum of the four phase shifts as we would expect from Eq. (2b). The different functions have been offset horizontally for clarity. (c) Transmission function $T(E)$. The solid curve represents the exact $T(E)$ calculated using the method described in Ref. 11. The crosses represent an approximate calculation based on the relation $T = \sin^2(\pi N_d/2)$.

it would change if we were to include a few gold atoms from the pads as part of the molecule. The gold atoms would then form the leads and not the sulphur atoms. But the current would still have to funnel through individual p_z orbitals giving only one nonzero phase shift per spin. In general, if there are M_{eff} number of nonzero phase shifts that are approximately equal then we can write

$$R^{-1} \approx (e^2/h) M_{\text{eff}} \sin^2(\pi N_d/M_{\text{eff}}), \quad (4)$$

which reduces to Eq. (3) if $M_{\text{eff}}=2$ corresponding to single-mode spin degenerate conduction.

Closed shell molecules: Most molecular wires that have been investigated so far involve closed-shell molecules for which N_d is an even number in the isolated state, and Eq. (3) predicts infinite resistance as we would expect. Connecting the molecule to the metallic pads has two distinct effects. Firstly, a fractional number (α_T) of electrons are transferred to or from the molecule depending on the work function of the metal. For the structure considered in this paper [Fig. 1(a)] we expect very little charge to be transferred into or out of the molecule since the work function of gold (5.3 eV) is slightly smaller than the average of the ionization potential

(8.3 eV) and the electron affinity (2.4 eV) of the molecule.¹⁷ Experimentally, the amount of charge transferred has been measured for many metal-molecule complexes and is usually quite small.

Secondly, connecting to the metallic pads makes the levels broaden, causing the highest occupied molecular orbital (HOMO) to lose a fraction of its electrons, since part of its spectrum now lies above the Fermi energy. The lowest unoccupied molecular orbital (LUMO), on the other hand, gains a fraction of electrons, since part of its spectrum lies below the Fermi energy. Assuming the HOMO to be an odd level and the LUMO to be an even level (the two usually have opposite parities), we can write ($\alpha_1 - \alpha_2 = \alpha_T$):

$$N_{\text{even}} = \text{Even integer} + \alpha_1$$

$$N_{\text{odd}} = \text{Even integer} - \alpha_1 \rightarrow R^{-1} = \frac{2e^2}{h} \sin^2 \frac{\pi(\alpha_1 + \alpha_2)}{2}.$$

If we assume the molecule to remain neutral ($\alpha_T = 0$) then α_1 and α_2 are equal. If we further ignore the effect of all the levels other than the HOMO and the LUMO then we can show that $\pi\alpha_1 = \pi\alpha_2 \approx 2\Gamma_0/E_g$, where Γ_0 is the total broadening of the HOMO and LUMO levels, E_g is the separation between them, and the ratio Γ_0/E_g is assumed to be much less than 1. With these approximations we can write

$$R^{-1} \cong (2e^2/h) (2\Gamma_0/E_g)^2.$$

This equation is often not accurate because it ignores all levels other than the HOMO and the LUMO. But it is still useful in a qualitative sense. It shows that the resistance of a neutral molecule is essentially determined by the parameter, Γ_0/E_g , equal to the ratio of the broadening to the band gap. This parameter can be adjusted through the functional groups that bind the molecule to the metallic contacts. A localized state in the middle of a molecule contributes very little to the conductance because it is hardly broadened by the coupling to the metal. The level broadening is also smaller for longer molecules because the clips at the ends represent a smaller perturbation. Longer molecules also have a smaller bandgap but usually the reduction in E_g is small compared to the reduction in Γ_0 , leading to an overall increase in resistance with length as noted by several authors.^{10,11}

Open-shell molecules: For an open-shell molecule with an odd number of electrons, N_d is an odd number. Equation (3) then predicts a low resistance even if the molecule is very weakly coupled. This is because the Fermi energy is pinned to the middle of a level leading to a large transmission regardless of the level broadening. In practice, however, if the level broadening Γ is small compared to the charging energy U then one enters the Coulomb blockade regime where conduction is suppressed by single-electron charging effects.¹⁸ This can be viewed as the molecular analog of the Mott transition that occurs in band conduction when the bandwidth becomes smaller than the charging energy. The question is whether Eq. (3) is still valid in this regime. To answer this question let us assume for simplicity that conduction takes place primarily through a single energy level. The problem is then analogous to the well-known ‘‘Anderson impurity’’ problem for which the transmission can be shown to be given by $T = n \sin^2(\pi N/n)$, N being the number of electrons occupying an n -fold degenerate level.¹⁸ It is well

known that if the charging energy U is large compared to the level broadening Γ then this relation is valid only at low temperatures when the transmission is due to the Kondo peak. But at temperatures that are high compared to the Kondo temperature, it is not valid as noted in Ref. 15. Similarly we would expect that in the regime $U \gg \Gamma$, Eqs. (3) or (4) would describe the Kondo peak and can be used if the resistance is measured *below the Kondo temperature*. But it is not relevant as far as the high-temperature resistance is considered. The problem is that in this ‘‘local moment regime’’ we cannot assume the phase shifts for the two spins to be equal, as we did in obtaining Eq. (3) from Eq. (2). Instead we obtain

$$R^{-1} = (e^2/h) [\sin^2(\pi N_{d,\uparrow}) + \sin^2(\pi N_{d,\downarrow})].$$

However, we will not consider this local moment regime further in this paper, assuming that the coupling of the molecules to the metallic pads is large enough that $\Gamma \gg U$.

Derivation of Eq. (2): For a symmetric molecule the S matrix $[s]$ can be written as

$$s = \begin{bmatrix} r & t \\ t & r \end{bmatrix} \rightarrow T = \text{trace}(t^+ t) = M - \text{trace}(r^+ r). \quad (5)$$

Each of the matrices t and r is of order $[M \times M]$. We can use a unitary transformation to transform the S matrix into the form

$$\tilde{s} = \frac{1}{2} \begin{bmatrix} I & I \\ I & -I \end{bmatrix} \begin{bmatrix} r & t \\ t & r \end{bmatrix} \begin{bmatrix} I & I \\ I & -I \end{bmatrix} = \begin{bmatrix} r+t & 0 \\ 0 & r-t \end{bmatrix}, \quad (6)$$

where $[I]$ and $[0]$ are the identity and null matrices, each of order $M \times M$. The matrix $[r+t]$ represents the S matrix for symmetry inputs that excite the leads on the two sides with the same sign, while the matrix $[r-t]$ represents the S matrix for antisymmetric inputs that excite the leads with opposite signs. The eigenstates of a symmetric molecule can also be classified as even and odd and we use N_{even} and N_{odd} to denote the total number of electrons occupying each group of states. We note that the even and odd subspaces are completely decoupled from each other so that we can apply the Friedel sum rule to *each part individually*:

$$\frac{1}{2} \arg(\det[r+t]) = \pi N_{\text{even}}$$

$$\text{and } \frac{1}{2} \arg(\det[r-t]) = \pi N_{\text{odd}}.$$

Combining the two relations we can write

$$\frac{1}{2} \arg(\det[r+t][r^+ - t^+]) = \sum_{m=1}^M \phi_m = \pi N_d, \quad (7)$$

where $N_d \equiv N_{\text{even}} - N_{\text{odd}}$

and $\exp[i2\phi_m]$ are the eigenvalues of the $(M \times M)$ matrix $[r+t][r^+ - t^+]$ (this can be taken as the formal *definition* of the phase shifts). We can write

$$\text{trace}([r+t][r^+ - t^+]) = \sum_{m=1}^M e^{i2\phi_m} \quad (8a)$$

$$\text{and } \text{trace}([r^+ - t^+][r+t]) = \sum_{m=1}^M e^{-i2\phi_m}. \quad (8b)$$

Adding Eqs. (8a) and (8b) we obtain

$$\text{trace}(r^+ r - t^+ t) = \sum_{m=1}^M \cos(2\phi_m). \quad (9)$$

Since $\text{trace}(r^+ r + t^+ t) = M$, we obtain

$$T \equiv \text{trace}(t^+ t) = \sum_{m=1}^M \sin^2 \phi_m. \quad (10)$$

Combining with Eq. (1) we obtain Eq. (2a). Equation (2b) is the same as Eq. (7) above.

Numerical Example: We now present a simple illustrative example based on a noninteracting Hamiltonian. As we have discussed, the molecule shown in Fig. 1(a) has eight modes in each lead: $M=8$. Figure 1(b) shows the four distinct phase shifts (due to spin degeneracy the phase shifts come in pairs that are equal) obtained from the eigenvalues of $[r^+ t][r^+ - t^+]$. The point to note is that three of the four phase shifts are nearly equal to zero in the energy range from -12 eV to -4 eV. This is because the conduction through the molecule in this energy range occurs primarily through the p_z orbitals of the sulphur and carbon atoms. The structure is thus effectively single moded and we can use Eq. (3) with good accuracy at least around the HOMO-LUMO gap.

In Fig. 1(b) we have also shown $N_d(E)$ (per spin), which is equal to the sum of the four phase shifts as we would expect from Eq. (2b). $N_d(E)$ is calculated as follows. We first obtain the eigenenergies of the molecule which are complex due to the coupling to the metallic contact: $E_i = \varepsilon_i + i\Gamma_i$. The imaginary part Γ_i determines the broadening of level “ i ” due to the coupling. Its magnitude depends on how effectively the level can empty into the metallic reservoir. Knowing ε_i and Γ_i , we can calculate N_{even} and N_{odd} :

$$N_{\text{even,odd}} = 2(\text{for spin}) \times \sum_{\text{even,odd levels}} [\vartheta(E - \varepsilon_i) - (1/\pi) \tan^{-1}(\Gamma_i/E - \varepsilon_i)]. \quad (11)$$

The first term (ϑ is the unit step function) gives the number of electrons that would be present if the molecule were isolated ($\Gamma_i=0$) while the second term gives the gain or loss due to the coupling to the contacts. This relation can be obtained simply by integrating a Lorentzian of width Γ_i centered around ε_i , but it is valid for non-Lorentzian line shapes too. It applies even to interacting many-body systems if we can identify the one-particle excitation energies (ε_i) and their escape rates (Γ_i).

Figure 1(c) compares the transmission calculated from Eq. (3) with the actual calculation.¹⁹ The agreement is excellent above -12 eV. The discrepancy below the HOMO at -12 eV is expected since all four phase shifts are significant in this energy range [see Fig. 1(b)] and Eq. (3) is not applicable.

Summary: We have presented a simple expression for the resistance of a symmetric molecule in terms of a set of M phase shifts which are related by a sum rule to $N_d = N_{\text{even}} - N_{\text{odd}}$, N_{even} and N_{odd} being the number of electrons occupying the even and odd eigenstates, respectively. This relation is based on the Friedel sum rule and as such should be valid even in the presence of interactions, as long as the broadening of the molecular levels due to the coupling to the leads is larger than any broadening due to interactions within the molecule. Many molecular wires of interest are effectively single moded, allowing us to write a particularly simple relation [Eq. (3)] that lends insight into the factors affecting the resistance of a molecule. A simple example is presented to illustrate the use of these relations.

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¹⁶Actually, the number of modes is even larger because the orbitals on the interior atoms have some coupling to the gold. Besides, we are ignoring the d orbitals. Formally one could say that the number of modes is determined by the number of orbitals that acquire an imaginary self-energy due to the coupling to the gold contact.

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¹⁹We use the method described in Ref. 11, taking proper account of the geometry of the gold-thiol bonds and the band structure of gold. However, unlike Ref. 11, we have left out the d orbitals completely.