Exact analytic formula for conductance predicting a tunable Sommerfeld-Arrhenius thermal transition within a single-step tunneling mechanism in molecular junctions subject to mechanical stretching

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We show that the conductance $G$ of molecular tunnel junctions wherein the charge transport is dominated by a single energy level can be expressed in closed analytic form which is exact and valid at arbitrary temperature $T$ and model parameter values. On this basis, we show that the single-step tunneling mechanism is compatible with a continuous thermal transition from a weakly $T$-dependent $G$ at low $T$ (Sommerfeld regime) to a nearly exponential $1/T$-dependent $G$ at high $T$ (Arrhenius-like regime). We predict that this Sommerfeld-Arrhenius transition can be observed in real molecular junctions and can be continuously tuned, e.g., via mechanical stretching.

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INTRODUCTION

As a rule, temperature independent conductance data measured in molecular junctions are interpreted as evidence of single-step charge transport by tunneling while a pronounced temperature dependent conductance is taken as indication of a two-step hopping mechanism [1–13]. Notable exceptions claiming a significant $T$ dependence of the transport by tunneling exist [14–23]. In nearly resonant cases ($|\varepsilon_0| \lesssim 0.1$ eV), temperature dependent currents can arise due to the thermal broadening of the electronic Fermi distribution in electrodes [14, 21]. Where experimentally available, the impact of the electrodes’ work function turned out to be extremely useful for discriminating whether the temperature dependence is due to transport by hopping or transport by tunneling [23]. Still, a thorough investigation to clarify this issue has not been attempted, and this is one of the main aims of the present work.

In our analysis, we will focus on the low bias conductance $G$ of a molecular junction wherein the charge transport is dominated by a single level (molecular orbital, MO). We report an analytic formula for $G$ which is exact and valid for arbitrary values of all relevant parameters (temperature $T$, MO-electrode couplings $\Gamma$’s, and MO energy offset $\varepsilon_0$ relative to electrodes’ Fermi energy).

Based on this exact expression, we are able to specify the parameter ranges wherein the transport by tunneling yields a $G$ strongly dependent on $T$. Pleasantly, these ranges turn out to comprise values characterizing real molecular junctions.

The presently deduced formula for $G$ predicts the possibility that, without changing the single-step transport mechanism, upon rising the temperature, a tunneling junction can continuously switch from a weakly $T$-dependent $G$ at low $T$ (Sommerfeld regime) to a nearly exponential $1/T$-dependent $G$ at high $T$ (Arrhenius-like regime). Furthermore, it predicts that in real junctions the location of this Sommerfeld-Arrhenius transition can be continuously tuned because $\Gamma$ and/or $\varepsilon_0$ can be controlled by a mechanical stretching force and/or via molecular orbital gating, respectively.

MODEL AND GENERAL FORMULAS

Applied to uncorrelated transport, the general Keldysh formalism [24–26] yields the following expression of the low bias conductance $G \equiv \partial I(V)/\partial V|_{V \to 0}$ of a single molecule tunneling junction at finite temperatures $T = 1/(k_B \beta)$ [27]

$$
\frac{G}{G_0} = -\int_{-\infty}^{+\infty} d\varepsilon \mathcal{T}(\varepsilon) \frac{\partial}{\partial \varepsilon} f(\varepsilon)
= \frac{\beta \Gamma^2}{4} \int_{-\infty}^{+\infty} \frac{d\varepsilon}{(\varepsilon - \varepsilon_0)^2 + \Gamma^2} \text{sech}^2 \frac{\beta\varepsilon}{2}
$$

(1)

Here $G_0 \equiv 2e^2/h = 77.48 \mu S$, $\mathcal{T}(\varepsilon)$, and $f(\varepsilon) = 1/(1 + e^{\beta \varepsilon})$ are the quantum conductance, transmission function, and Fermi distribution, respectively, and energies are measured relative to electrodes’ Fermi energy ($E_F \equiv 0$). Eq. (1) assumes a single level (MO) of energy $\varepsilon_0$ whose coupling to two flat wide band $s$(ubstrate) and $t$(ip) electrodes is
quantified by an effective coupling \( \Gamma_g \) expressed in terms of the individual strengths \( \Gamma_s \) and \( \Gamma_t \)
\[
\Gamma_g^2 = \Gamma_s \Gamma_t \propto \tau_s^2 \tau_t^2 \tag{2a}
\]
which also give rise to a smeared Lorentzian-shaped transmission of finite half-width \( \Gamma_a \)
\[
\Gamma_a = (\Gamma_s + \Gamma_t)/2 \tag{2b}
\]
In general, the MO-electrode exchange integrals are different \((\tau_s \neq \tau_t)\), which make the geometric and arithmetic averages different from each other \((\Gamma_g \leq \Gamma_a)\).

Integration by parts of Eq. (1) followed by contour integration yields the following general formula for the conductance in terms of the real part of the trigamma function \( \psi(t) \) in terms of the real part of the trigamma function
\[
\frac{G}{G_0} = \frac{\Gamma_g^2}{2\pi i k_B T} \text{Re} \psi' \left( \frac{1}{2} + \frac{\Gamma_i + i \varepsilon_0}{2\pi k_B T} \right) \tag{3}
\]
Recall that the trigamma function is defined as the derivative of the digamma function, \( \psi'(z) = \frac{d}{dz} \psi(z) \), which, in turn, is the logarithmic derivative of Euler’s gamma function \(\gamma(\cdot)\).

Noteworthily, Eq. (3) is an exact result valid at arbitrary values of all parameters \((\varepsilon_0, \Gamma_g, \Gamma_a, \text{and } T)\) The well known low temperature limit \((k_B T \ll \Gamma_a) \) \([24, 51]\)
\[
\frac{G}{G_0} \bigg|_{k_B T \ll \Gamma_a} \approx \frac{\Gamma_g^2}{\varepsilon_0^2} \tag{4}
\]
follows from Eq. (3) by virtue of the asymptotic trigamma’s expansion \([30]\). Above, the zero temperature conductance \(G_{0K} \equiv G(T)|_{T=0} \) should not be confused with the conductance quantum \(G_0\).

In the opposite limit \((\Gamma_a \ll \pi k_B T, \text{Re } \varepsilon \rightarrow 1/2)\), the RHS of Eq. (3) reduces to
\[
\frac{G}{G_0} \bigg|_{\Gamma_a \ll \pi k_B T} = \frac{\pi}{4} \frac{\Gamma_g^2}{\Gamma_a k_B T} \text{sech}^2 \frac{\varepsilon_0}{2 k_B T} \tag{5a}
\]
which in a more particular limit acquires an Arrhenius-like form
\[
\frac{G}{G_0} \bigg|_{\varepsilon_0 \ll \pi k_B T} = \frac{\pi \Gamma_g^2}{\Gamma_a k_B T} \exp \left( -\frac{|\varepsilon_0|}{k_B T} \right) \tag{5b}
\]
The particular results of Eqs. (5a) and (5b) were first reported in refs. [27] and [16], respectively. Eq. (5a) is a limiting case of a more general approximate interpolation formula deduced earlier \([27]\) for \(\Gamma_{s,t} = \Gamma_{g,a} \) and parameter values where the peaks of \(T(\varepsilon)\) and \(-\partial T(\varepsilon)/\partial \varepsilon\) are sufficiently narrow and well separated from each other \([27]\).

Although exact and general, Eq. (3) may pose certain practical problems for experimental data processing. Special functions (read trigamma function \(\psi'(z)\)) having furthermore a complex argument are not usually implemented in data fitting softwares routinely employed by experimentalists.

Attempting to meet the legitimate experimentalists’ desire of having a formula merely containing elementary functions of real arguments, we arrived at the following very accurate approximation \((y \equiv \varepsilon_0/(2\pi k_B T))\)
\[
\frac{G}{G_0} \simeq \frac{\pi \Gamma_g^2}{4 \Gamma_a k_B T} \text{sech}^2 \pi y + \left( \frac{\Gamma_g}{2 \pi k_B T} \right)^2 \varphi(y) \tag{6a}
\]
\[
y \equiv \frac{\varepsilon_0}{2\pi k_B T}
\]
\[
\varphi(y) = \frac{y^2 - 34.7298}{(y^2 + 2.64790)^2} + 37.262 \frac{y^2 + 1.12874}{(y^2 + 2.17786)^2} + 3.01373 \frac{y^2 - 0.082815}{(y^2 + 0.25014)^3} \tag{6b}
\]
Notice the factor 4 entering denominator of the first term in the RHS of Eq. (6a); it replaces the wrong factor 16 (a typo) entering Eq. 6 of ref. [32]. Thorough tests in broad parameter ranges of experimental interest revealed that Eq. (6) — which embodies insight gained from series expansions, asymptotic behavior, and recurrence properties of the trigamma function — reproduces remarkably well the conductance computed exactly using Eq. (3). To exemplify, suffice it to say that, in all the figures presented below, the curves generated via Eqs. (5) and (6) cannot be distinguished from each other within the drawing accuracy.
RESULTS

It is evident that Eq. (3) predicts a tunneling conductance dependent on temperature. Still, the practically relevant question is whether the predicted dependence on $T$ is sufficiently strong for inferring a single-step tunneling mechanism based on transport data measured in real molecular junctions \cite{14,21,23}.

To answer this question, we used Eq. (3) to compute the conductance excess $\delta g \equiv G_{RT}/G_{0K} - 1$ at room temperature ($RT = 298.15$ K) relative to the zero temperature limit. Results of these numerical calculations are depicted in Fig. 1. To facilitate understanding Fig. 1, we note the following. There is no practically relevant dependence of $G$ on $T$ for molecular junctions (as experimentally demonstrated in junctions based on alkanes \cite{33,34}) with MO offsets $|\varepsilon_0| \sim 1$ eV \cite{35} much larger than thermal energies $\sim k_B T_{RT} = 25.7$ meV. Eq. (3) confirms that in such cases the conductance thermal excess is altogether negligible $\delta g \simeq 0$. The smallest value ($|\delta g| = 0.1 \Leftrightarrow G_{RT}/G_{0K} = 1.1$) on the $y$-axis in Fig. 1 corresponds to the lowest excess that can still be distinguished from very good statistical variances ($\sim 10\%$) inherently present in experiment \cite{35}. Depending on the value of $G_{RT} = 1$; $10$; $100$ pS, this conductance excess corresponding to an MO offset $|\varepsilon_0| = 0.409; 0.381; 0.355$ eV is depicted by the rightmost point on the green, red, and blue curves of Fig. 1, respectively. Higher conductance thermal excess requires smaller MO offsets. At the other extreme value ($|\delta g| = 99 \Leftrightarrow G_{RT}/G_{0K} = 100$) in Fig. 1, the MO offsets amounting to $|\varepsilon_0| = 0.254; 0.231; 0.197$ eV correspond to the leftmost points on the green, red, and blue curves, respectively.

MO energy offsets estimated for real molecular junctions fabricated with Zn-porphyrin \cite{16,18}, diarylethene \cite{22,37}, and perylene diimide \cite{23} fall in the above range ($|\varepsilon_0| \approx 0.15 - 0.35$ eV). Even smaller values $|\varepsilon_0| \approx 50$ meV were estimated for alkanedithiolates functionalized with ferrocene \cite{21,27}. For all aforementioned cases the transport data were found to be temperature dependent. For obvious physical reasons, a significant dependence $G = G(T)$ implies a sufficiently narrow transmission peak (i.e., a small $\Gamma_a$). Curves for $\Gamma_a$ versus $\varepsilon_0$ at given values of the RT conductance excess are depicted in Fig. 1.

The important message conveyed by Fig. 1 should be clear: orders of magnitude conductance enhancement upon increasing temperature is fully compatible with the single-step tunneling mechanism, backing the suggestions put forward in the experimental studies cited above.

Using parameter values extracted from data measured for n-type perylene diimide (PDI) molecular junctions with isocyanide surface linkers estimated earlier \cite{23}, further important predictions of the presently deduced Eq. (3) are collected in Fig. 2.

Fig. 2a reveals a crossover from a thermally activated conductance exhibiting an Arrhenius-type nearly exponential variation with $1/T$ at higher temperatures to a nearly $T$-independent $G$ at lower temperatures. The high-$T$ limit is approximately described by Eq. (5). For the approximate description of the low temperature range, the Sommerfeld expansion \cite{35,39} can be used. The expansion of the transmission function around $\varepsilon = 0$ in the RHS of Eq. (11) yields in this (Sommerfeld) regime the following expression valid to order $\mathcal{O}(T^4)$

$$
\frac{G}{G_0} \simeq \frac{\Gamma_a^2}{\varepsilon_0 + \Gamma_a^2} \left[ 1 + \frac{\varepsilon_0^2 - \Gamma_a^2/3}{(\varepsilon_0^2 + \Gamma_a^2)^2} (\pi k_B T)^2 \right]_0^{\Gamma_a \ll |\varepsilon_0|} \frac{\Gamma_a^2}{\varepsilon_0^2} \left( 1 + \frac{\pi^2 k_B T^2}{\varepsilon_0^2} \right)
$$

(7)

The inspection of Fig. 2a reveals that for the specific junctions envisaged an Arrhenius-Sommerfeld crossover should be observable at “reasonable” temperatures ($T \sim 170$ K). Although outside the narrow range explored in actual measurements \cite{23} ($247$ K $< T < 298$ K, cf. vertical lines in Fig. 2a), the prediction of such moderately low transition temperatures should encourage efforts for experimental observation.

Importantly, the present results for the tunneling conductance also predict that the location of the Arrhenius-Sommerfeld transition can be tuned. Two possibilities to achieve tunability are indicated in Figs. 2 by tuning the MO energy $\varepsilon_0$ (Fig. 2b) and by tuning the MO-electrode couplings $\Gamma_{s,t}$ (Fig. 2c). The former can be practically realized via molecular orbital gating \cite{33,40,41}. For the latter, molecular junctions subject to mechanical deformation are very appealing. As shown recently \cite{36,42}, the MO-electrode couplings are highly sensitive to an applied stretching force; $\Gamma$’s are primarily responsible for the observed conductance variations on orders of magnitude \cite{36,42}. This route to unravel an Arrhenius-Sommerfeld transition may also be relevant for the transport through artificial nanoarrays \cite{40,41} wherein the exchange integrals $\tau$’s on which the MO-electrode couplings $\Gamma$’s depend (cf. Eq. 2a) can be tuned in broad ranges.

Because, after all, the thermal transition between the Sommerfeld and Arrhenius-like regimes discussed above is a theoretical prediction, we do not want to end this section before justifying why, above, we have implicitly suggested
FIG. 1: (a) Conductance thermal excess at room temperature (RT) relative to zero temperature $\delta g \equiv G_{RT}/G_{0K} - 1$ as a function of the MO energy offset $|\varepsilon_0|$ for several values of the RT conductance $G_{RT}$. (b) Curves for the transmission halfwidth $\Gamma_a$ versus $\varepsilon_0$ for a given value of $\delta g$ (ranging from 0.1 to 100) indicated for each curve. Dashed lines correspond to several values of $G_{RT}$ computed by assuming $\Gamma_g = \Gamma_a \equiv \Gamma$.

N-type perylene diimide (PDI) molecular junctions with isocyanide surface linkers subject to mechanical stretching as promising candidates for the practical realization of a tunable Arrhenius-Sommerfeld transition.

Reference to PDI-based junctions within the present analysis entirely based on the single-step scenario was not accidental for three reasons:

1. First, because it was demonstrated that in these junctions the impact of the contact metallurgy elaborated experimentally in Frisbie’s group on the activation energy safely rules out a two-step hopping scenario [23];

2. Second, because the foregoing analysis unraveled that in these junctions the temperature range (around $\sim 170$ K) wherein the Sommerfeld-Arrhenius transition is expected should pose no special experimental problems;

3. Third, because studying PDI-based junctions at variable stretching force should be experimentally feasible. Molecular junctions under mechanical deformation is routine technique [36, 42, 48, 49] and topic of continuing interest in the same Frisbie’s group where the transport through PDI-based junctions at variable temperature to which we referred in the present analysis was recorded.

CONCLUSION

In closing, the present paper emphasizes that a two-step hopping transport mechanism should by no means taken for granted merely because $G$ versus $1/T$ data follow an Arrhenius pattern.
FIG. 2: (a) Results for conductance obtained using parameters characterizing molecular junctions based on perylene diimide (PDI) beyond the range (indicated by magenta vertical lines) sampled in measurements indicate the occurrence of a gradual Arrhenius-Sommerfeld transition at experimentally accessible temperatures ($T \sim 170$ K). (b, c) Results showing how the Sommerfeld-Arrhenius transition (depicted by dashed ellipses) can be tuned in junctions subject to a mechanical stretching force or via molecular orbital gating.
The exact analytic formula for the single-step tunneling conductance \( G \) deduced in this work demonstrates that molecular junctions wherein charge transport proceeds via single-step tunneling can undergo a tunable transition from an Arrhenius-type strongly temperature dependent regime to a weakly temperature dependent Sommerfeld regime.

Based on this formula, we predicted that molecular junctions subject to variable stretching force or molecular orbital gating represent possible realizations of the tunable Sommerfeld-Arrhenius transition and hope to encourage accompanying experimental efforts in this direction.

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