Molecular charge transport : relating orbital structures to the conductance properties

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THE SIMMONS MODEL

Full formulation of the Simmons formula. According to ref [1], a full expression for the current density, J, through a barrier between two similar metal electrodes over the entire voltage range is given by:

$$
\begin{aligned}
J &= c\{\tilde{A}+\tilde{B}+\tilde{C}\} \\
c &= \frac{4\pi me}{h^3} \\
\tilde{A} &= eV\int_0^{\eta-eV} exp(-A\sqrt{\eta+\bar{\phi}-E_x})dE_x \\
\tilde{B} &= -\bar{\phi}\int_{\eta-eV}^{\eta} exp(-A\sqrt{\eta+\bar{\phi}-E_x})dE_x \\
\tilde{C} &= \int_{\eta-eV}^{\eta}(\eta+\bar{\phi}-E_x)exp(-A\sqrt{\eta+\bar{\phi}-E_x})dE_x.
\end{aligned}
$$

Here, $A=(4\pi\Delta s/h)\sqrt{2m}$, where $\Delta s = s_2 - s_1$ is the width of the barrier at the Fermi energy of the metal and $\bar{\phi}$ is the average barrier height. In ref [1], parts of the integrands are neglected. The consequence of this is that for small A and/or small ϕ, the commonly used Simmons expression gives unphysical results. Below, we calculate the full integrands.
$\tilde{A}$ and $\tilde{B}$ are of the same form:

$$-\int_{e_1}^{e_2} exp(-A\sqrt{\eta+\bar{\phi}-E_x})d(-E_x)>0$$

By substituting $y^2 = \eta + \bar{\phi} - E_x$ and $d(-E_x) = d(\eta + \bar{\phi} - E_x) = dy^2 = 2ydy$, this becomes:

$$-\int_{y_1}^{y_2} exp(-Ay) \cdot 2ydy$$

Here, $y_{1,2} = \sqrt{\eta + \bar{\phi} - e_{1,2}}$. These integrals can be solved by partial integration [1]. Boundaries for $\tilde{A}$ are $e_1 = 0$, $e_2 = \eta - eV$, $y_1 = \sqrt{\eta + \bar{\phi}}$, $y_2 = \sqrt{\bar{\phi} + eV}$, yielding:

$$\tilde{A} = \frac{2eV}{A^2}\{(A\sqrt{\bar{\phi} + eV} + 1)exp(-A\sqrt{\bar{\phi} + eV}) - (A\sqrt{\eta + \bar{\phi}} + 1)exp(-A\sqrt{\eta + \bar{\phi}})\}.$$

Boundaries for $\tilde{B}$ are $e_1 = \eta - eV$, $e_2 = \eta$, $y_1 = \sqrt{\bar{\phi} + eV}$, $y_2 = \sqrt{\bar{\phi}}$, yielding:

$$\tilde{B} = \bar{\phi}\frac{2}{A^2}\{(A\sqrt{\bar{\phi}} + 1)exp(-A\sqrt{\bar{\phi}}) - (A\sqrt{\bar{\phi} + eV} + 1)exp(-A\sqrt{\bar{\phi} + eV})\}.$$

Like $\tilde{A}$ and $\tilde{B}$, $\tilde{C}$ can again be solved by substituting $y^2 \equiv \eta + \bar{\phi} - E_x$ and $d(-E_x) = d(\eta + \bar{\phi} - E_x)$ and partial integration.

$$\tilde{C} = -2\int_{y_1}^{y_2} y^3 exp(-Ay)dy$$

Boundaries for $\tilde{C}$ are $e_1 = \eta - eV$, $e_2 = \eta$, $y_1 = \sqrt{\bar{\phi} + eV}$, $y_2 = \sqrt{\bar{\phi}}$, so that:

$$\begin{aligned}\tilde{C} &= \frac{2}{A}\{(\bar{\phi}^{3/2} + \frac{3}{A}\bar{\phi} + \frac{6}{A^2}\sqrt{\bar{\phi}} + \frac{6}{A^3})exp(-A\sqrt{\bar{\phi}}) \\ &\quad -((\bar{\phi} + eV)^{3/2} + \frac{3}{A}(\bar{\phi} + eV) + \frac{6}{A^2}\sqrt{\bar{\phi} + eV} + \frac{6}{A^3})exp(-A\sqrt{\bar{\phi} + eV})\}\end{aligned}$$

Taking all integrals together, we can calculate J. Note that for relatively high and/or thick barriers, i.e. if $A\sqrt{\phi \pm eV} \gg 1$, the full expression for J reduces to eq. (26) of reference [1]:

$$\begin{aligned}J &= J_0\{(\phi - eV/2)exp(-A\sqrt{\phi - eV/2}) - \\ &\quad (\phi + eV/2)exp(-A\sqrt{\phi + eV/2})\}.\end{aligned}$$

where, $J_0 = e/(2\pi hs^2)$.

Figure 1 shows V_m versus 1/d for each of the three equations mentioned above; eq. 26 of ref [1], (black), eq. 1 (Stratton) in the main text (blue) and the full Simmons expression (red). For thick barriers all three collapse on a single line. The maximum deviation between the three is in the order of a few percent for thin barriers (around $d = 5$Å). These differences are negligible compared to the spread in the experimental data as discussed in the Letter.

REFERENCES

[1] J. G. SIMMONS, *Generalized Formula For Electric Tunnel Effect Between Similar Electrodes Separated By A Thin Insulating Film*, Journal Of Applied Physics **34**, 1793 (1963).