Prominent nonequilibrium effects beyond the standard density functional theory approach in molecular electronic devices

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Table 1. The zero-bias conductance (in unit of $0.01G_0$) of Si_n-S-M (n=3,6,7; M=Ag,Au) calculated by TranSIESTA and SMEAGOL.

Package \ n		n=3 (Si_3)	n=6 (Si_6)	n=7 (Si_7)
TranSIESTA	M=Ag	4.55	2.15	1.61
	M=Au	5.40	2.97	1.89
SMEAGOL	M=Ag	4.50	2.14	1.61
	M=Au	5.45	2.99	1.85

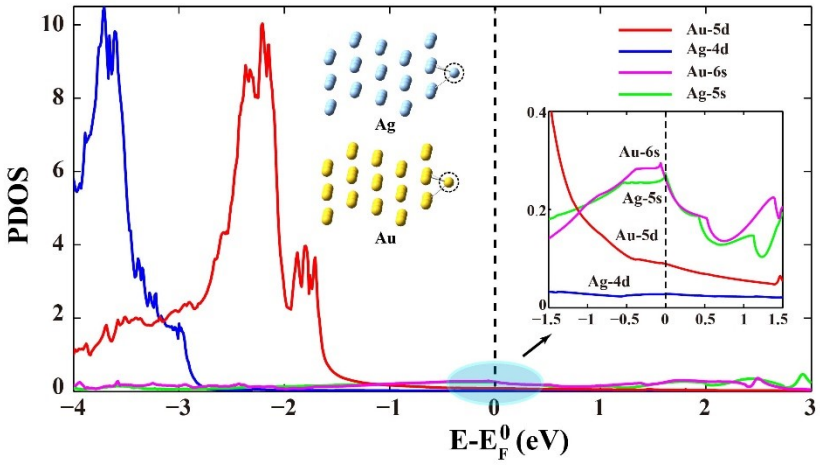

Figure 1. The local density of states projected onto the 6s and 5d orbitals of Au atom and the 5s and 4d orbitals of Ag atom that form bonds with silanes. Inset: Enlarged PDOS near the Fermi energy.

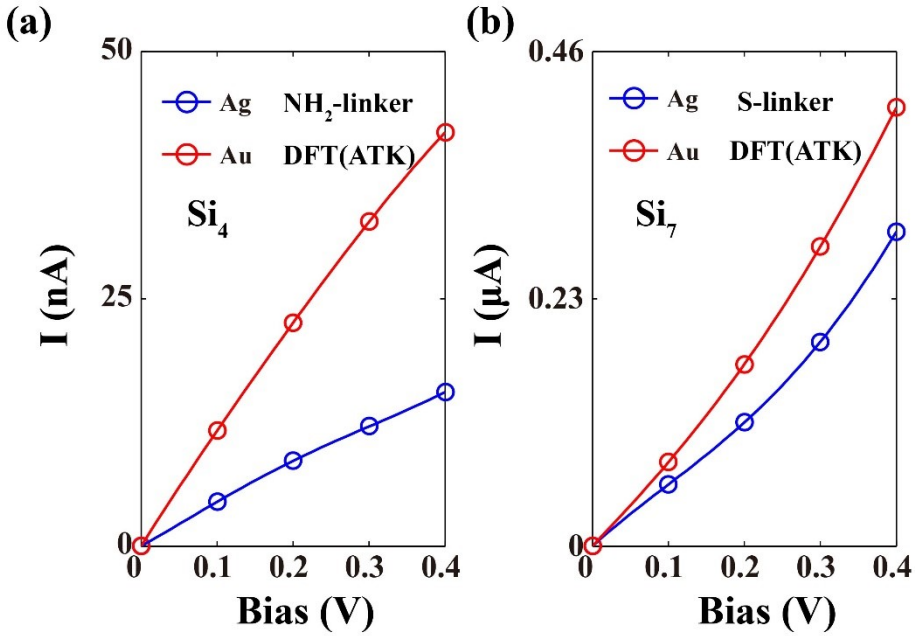

Figure 2. I-V curves calculated from ATK for **(a)** Si_4-NH_2-M (M=Au or Ag) and **(b)** Si_7-S-M (M=Au or Ag). In both cases, Au contact provide much higher conductivity than Ag.

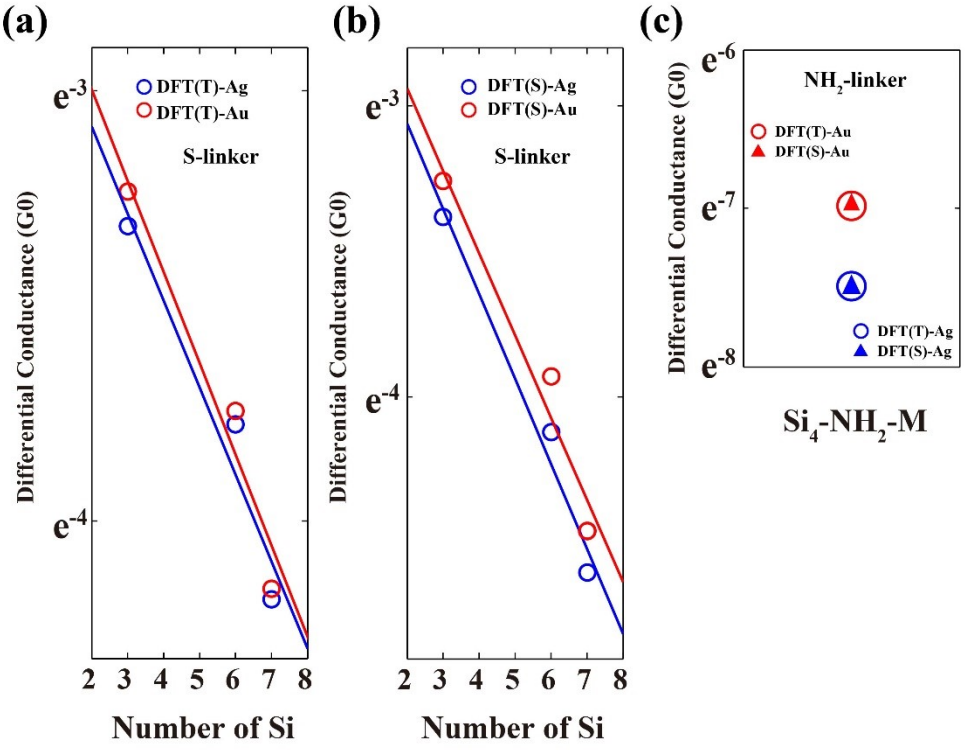

Figure 3. The differential conductance of the thiol-terminated silanes junctions Si_n-S-M (M=Au or Ag) at 0.2V calculated from **(a)** TranSIESTA (DFT(T)) and **(b)** SMEAGOL (DFT(S)). The solid lines show the linear fits to the data. **(c)** The differential conductance at 0.2 V for Si_4-NH_2-M (M=Au or Ag) from both DFT(T) and DFT(S). For NH_2 linker, they agree with each other (also agree with SS-DFT) remarkably well.

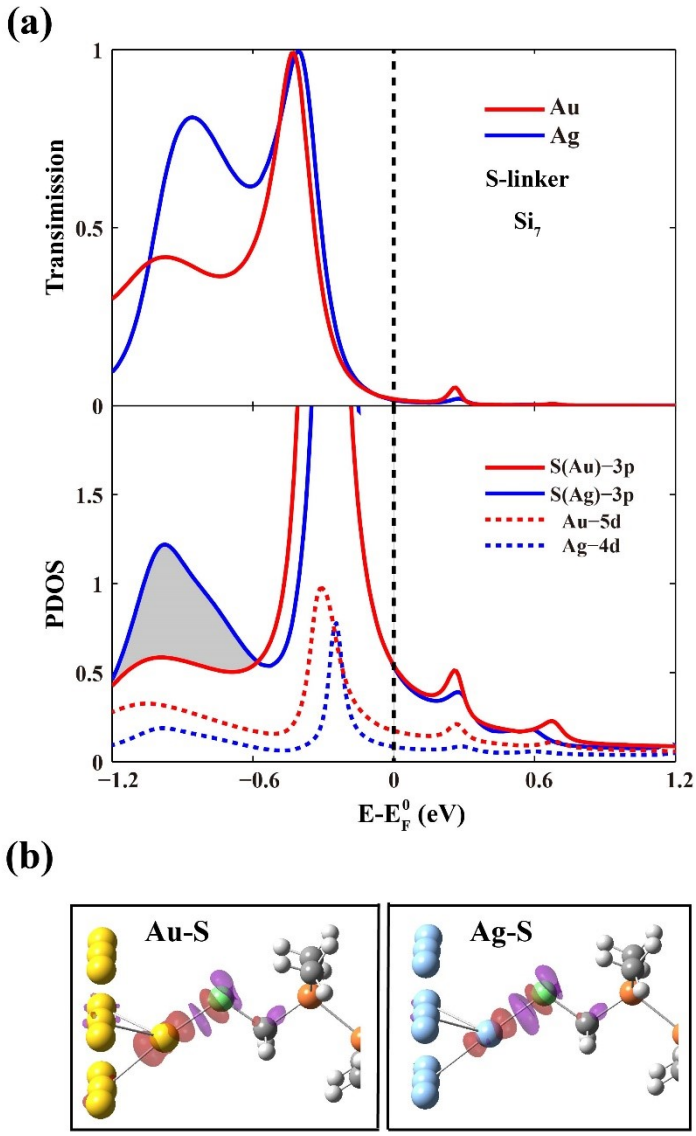

Figure 4. (a) The zero-bias transmission spectra of junctions Si_7-S-M (M=Au or Ag) (Upper panel) and the projected density of states (PDOS) of p orbital of the S atom and d orbital of Au/Ag atom binding with S (lower panel). S(Au or Ag) denotes the S atom binding with Au or Ag electrode. (**b)** The iso-surface (0.004e) of the density redistribution due to the metal-S bonds in the Si_7-S-M junctions. The purple (red) indicates the accumulation (depletion) of electrons. We can see clearly that the S atom gains more electrons from Ag than from Au.

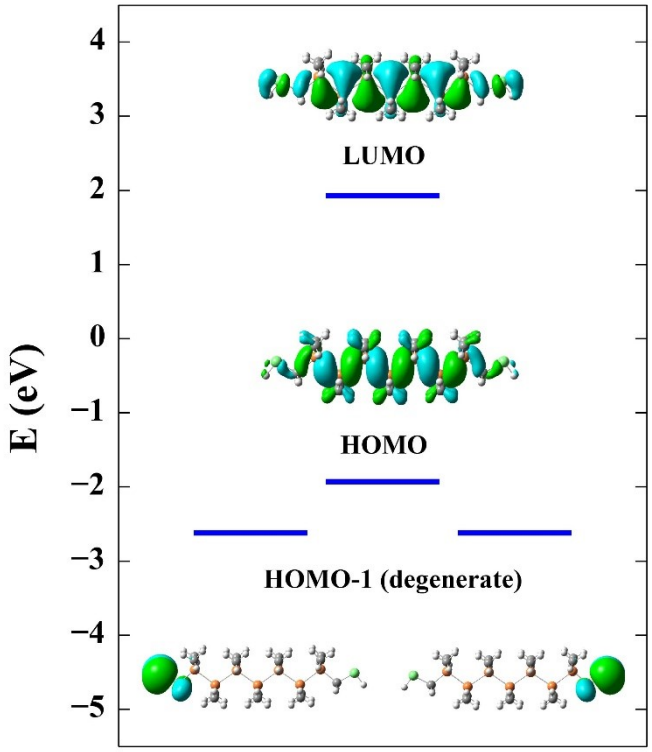

Figure 5. Frontier molecular orbitals of the thiol-terminated Silanes Si_7-SH. Note that two HOMO-1 orbitals are degenerate.

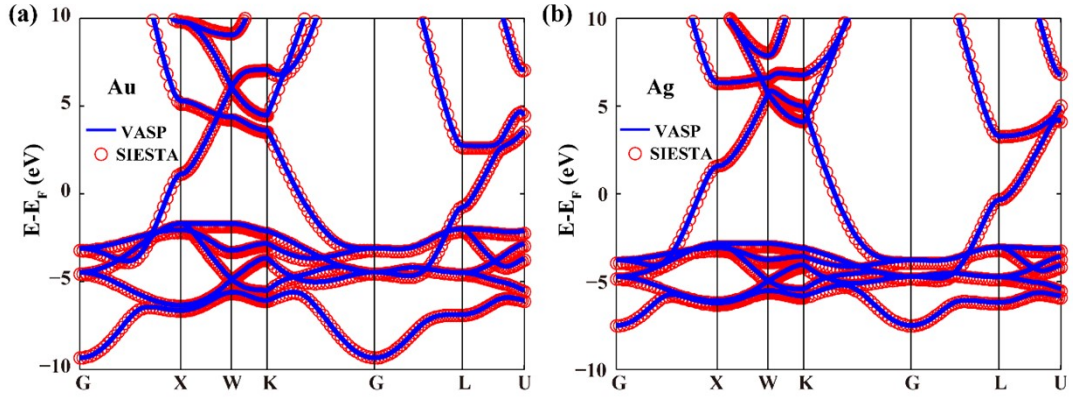

Figure 6. The band structures of bulk **(a)** Au and **(b)** Ag computed by VASP (in blue solid lines) and SIESTA (with red open circles) respectively in the first Brillouin zone. In both plots, the Fermi level was set to 0.0 eV.

Table 2. HOMO-LUMO gaps for amine-terminated and thiol-terminated silanes from SIESTA and VASP (in unit of eV). Two packages agree with each other well.

Molecule / Package	Si_4-NH_2	Si_3-SH	Si_6-SH	Si_7-SH
SIESTA	4.12	4.58	4.07	3.86
VASP	3.98	4.41	3.90	3.68