Evaluation of Basis Sets with 11-Electron Analytic Effective Core Potentials of Gold for Modeling Molecular Electronic Devices

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Three types of 11-electron analytic effective core potentials (ECPs) and their corresponding double-ζ and single-ζ basis sets of gold are evaluated using density functional theory (DFT) calculations. We find that, compared with basis sets derived for use with Hatree−Fock-based Los Alamos (LANL1) and Ermler−Christiansen (EC) ECPs, the DFT-derived Troullier−Martins (TM) ECP together with a single-ζ basis set (TMSZ) is more suitable to describe not only the interaction between gold atoms with a benzene-1,4-dithiolate molecule but also the electronic structure of an infinite 1-dimensional monatomic gold chain. Hence, TMSZ is the best single-ζ basis set with an 11-electron ECP for gold available currently to be used in theoretical calculations on electrical properties of molecular electronic devices with DFT based Green's function method employing a finite analytic basis of local orbitals.

1. Introduction

Following the continuous miniaturization of microelectronic devices, a great deal of attention has been devoted to molecular electronic devices in recent years.[1,2] A basic question that needs to be addressed before the fabrication of actual molecular electronic devices is how we can construct, measure, and understand the conductance of a molecule connected to two metallic electrodes. At present, both experimental and theoretical investigations on current−voltage characteristics of such molecular junctions have been extensively performed,[3−26] for example, on gold−dithiomolecule−gold transport junctions. It is a great challenge for theoretical calculations to replicate experimental results exactly since both the molecule and the semiinfinite leads in these junctions must be properly described simultaneously. It is well-known that the current through the molecular junction is influenced by the quantum nature of the molecule, the coupling between the molecule to the electrodes, and the electronic properties of the electrodes near the Fermi energy level.[1,13] Though solving the Lippmann−Schwinger equation with plane waves is used to evaluate the junction conductance,[7,8] the density functional theory (DFT) based Green's function method employing a finite set of local orbitals is more prevalent.[9−26] In the latter approach, two approximations are always introduced: the first one is that the exact, non-Hermitian, energy-dependent, many-body self-energy operator is approximated by the energy-independent, real DFT exchange-correlation potential; the second one is that the Green's function is expanded in terms of a finite, incomplete basis set. Hence, not only must an appropriate exchange-correlation functional be selected, but the choice of basis sets also plays a critical role in determining the coupling strength and electronic structures of metal electrodes.

From practical considerations, gold is the most popular one among all electrode materials, because stable molecular junctions can be constructed using the Au−S bond or the Au−N bond.[4,6] Since most physical and chemical properties of molecules and solids are dominated by valence electrons, the effect of the core electrons can be represented by an effective core potential (ECP) that significantly reduces the size of the basis set needed to treat the molecule and solid, which will decrease the computational effort considerably. Furthermore, once derived from relativistic calculations, ECP will include relativistic effects even if nonrelativistic theory is applied to valence electrons.[27] For gold, the 5s and 5p atomic levels are well below the 5d level, whereas the sp−d hybridization effect between the 5d and 6s, 6p atomic orbitals is important for electronic properties near the Fermi level and contributes to bonding in the bulk and at surfaces. Therefore, it is a reasonable choice to treat 5s and 5p states together with lower lying ones as the core, which leads to an 11-electron ECP. Even so, the calculation of Green's function is still very expensive with a large basis set because many gold atoms should be included in the extended molecule to determine the lineup of molecular levels relative to the Fermi level of gold electrodes correctly.

The performance of an ECP usually depends on the method by which it is derived. Certainly, just as pointed out by Alkauskas et al.,[27] the smaller the core, the less important is the derivation method. In the limit of a bare nucleus, the potential becomes $\sim 1/r$, which is of course independent of the method. The comparison between ECPs derived from Hatree−Fock (HF) atomic calculations and DFT-based ECPs has been done previously, which has proved that HF-based ECPs can give good prediction in DFT calculations.[28] However, their comparison is limited in small core ECPs with a common, large basis set appropriate for the all-electron case, which will increase computing time and storage at a cost that is not justified for our purpose because electron transport in molecular electronic devices occurs within an energy range of several electonvolts around the Fermi level. Therefore, 11-electron ECPs represent the best compromise. In calculations of the molecular junction conductance employing a very efficient electronic structure code GAUSSIAN, two 11-electron HF-based ECPs with their corresponding single-ζ basis sets are often used,[9−12,19−21] namely,

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Ermler−Christiansen ECP and Los Alamos 11-electron ECP,[29−31] which are respectively designated as EC and LANL1. Both these ECPs and their corresponding basis sets are derived from reference calculations on an isolated gold atom within scalar-relativistic (SR) Dirac−Fock theory. However, their applicability to modeling molecular electronic devices with DFT calculations has not been well tested. Recently, Alkauskas, Baratoff, and Bruder developed a new 11-electron ECP for gold derived from DFT-based Troullier−Martins (TM) pseudopotential,[27,32] and they also derived two compact basis sets, (3s3p3d)/[1s1p1d] (TMSZ) and (6s6p5d)/[2s2p2d] (TMDZ). All-electron DFT calculation on atomic Au is performed in the spin-restricted formalism with the gradient-corrected Becke's exchange functional and the LYP correlation functional (BLYP).[33,34] In this paper, using a Au−benzene-1,4-dithiolate (BDT)−Au complex molecule and a 1-dimensional (1D) monatomic gold chain as testing models, DFT calculations are employed to compare these basis sets to see which is the best one describing both the coupling of gold atoms with organic molecules and electronic structures of gold periodic structures.

2. Calculation Method

DFT calculations with the BLYP functional are performed using the GAUSSIAN 03 program package.[35] The all-electron 6-31G(d) basis set is used for S, C, and H atoms.[36] For gold, we used basis functions recommended in the original papers on the corresponding ECPs. Since using small-core ECPs can minimize errors in the treatment of electron correlation, we chose two types of 19-electron ECP basis sets, LanL2DZ and SDD, as the reference level of approximation. LANL2 is a so-called shape-consistent ECP, containing no adjustable parameters.[37] On the contrary, SDD is an energy-consistent ECP that is constructed to reproduce some representative experimental data of a single atom.[38] The standard ECP basis sets included as part of the Gaussian 03 package are SDD, LANL2DZ, LANL2MB, LANL1DZ, and LANL1MB, respectively. For the LANL1 basis set, Xue and co-workers made another choice in their calculations,[19−21] i.e., they deleted the most diffuse s, p, and d primitives from the associated valence basis set and contracted the remaining primitives to a minimal basis set, which is termed LanL1(2s2p2d)/[1s1p1d]. In the case of the EC ECP, both the original (3s3p4d) basis set and the contracted (3s3p4d)/[1s1p1d] basis set are used,[29,30] which are called "ECPB" and "ECMB" for short, respectively. The Au-BDT-Au complex was optimized without constrains, and the charge transfer and the bonding nature of the Au−S bonds are illustrated using natural bond orbital (NBO) analysis.[39−41] Electronic structures of the 1D monatomic gold chain were calculated using the periodic boundary conditions (PBC) algorithm of Gaussian 03;[42,43] 59 k points sampling in the 1D Brillouin zones were employed. Since our aim in this work is not to compare the performance of different ECPs, but rather to find a small basis set with its corresponding ECP suitable for modeling molecular electronic devices, only the single-ζ basis set of each ECP is well tested.

3. Results and Discussion

3.1. Single Gold Atom. Table 1 shows Kohn−Sham eigenenergies of an isolated Au atom calculated in the spin-unrestricted formalism. The energy difference between the 5d and 6s atomic orbitals calculated using the 19-electron SDD basis set is less than 1 eV, whereas LANL2DZ slightly overbinds d-states.[37] Among all basis sets with an 11-electron ECP, only TMDZ and TMSZ work quite well, both of them giving an energy difference comparable to that of SDD. LANL1DZ, LANL1MB, ECPB, and ECMB all underbind the s-state and overbind d-states, giving rise to a very large s−d difference, which will lead to a poor description of sp−d hybridization in polyatomic systems. The performance of LanL1(2s2p2d)/[1s1p1d] is even worse, the calculated highest occupied atomic orbital is not the 6s orbital whose energy is as high as 65.06 eV; the calculated highest occupied atomic orbital is one of the 6p orbitals with an eigenenergy of 1.12 eV, still higher than the vacuum level. These errors arose from the arbitrary removal of the most diffuse s, p, and d primitives from the valence basis set; the new compact basis set cannot correctly describe a neutral gold atom in its ground state.

TABLE 1: Comparison of Kohn−Sham Eigenenergies of a Single Au Atom in the Ground State

	$\epsilon_{5d\uparrow}$ (eV)	$\epsilon_{5d\downarrow}$ (eV)	$\epsilon_{6s\uparrow}$ (eV)
SDD	−6.94	−6.70	−5.94
LANL2DZ	−7.14	−6.92	−6.07
LANL2MB	−5.98	−5.76	−5.68
TMDZ	−6.91	−6.64	−5.95
TMSZ	−6.97	−6.68	−5.95
LANL1DZ	−8.89	−8.66	−4.81
LANL1MB	−10.28	−10.03	−5.25
LANL1(2s2p2d)/[1s1p1d]	−4.17	−4.02	65.06
ECMB	−10.22	−9.96	−3.22
ECPB	−9.32	−9.17	−4.21

TABLE 2: Comparison of Au−S Bond Lengths, Atomic Charge on Au Atoms, and Binding Energies of the Optimized Au-BDT-Au Complex

	bond length (Å)	atomic charge	BE (eV)
SDD	2.33	0.16	2.78
LANL2DZ	2.35	0.18	2.62
LANL2MB	2.38	0.16	2.44
TMDZ	2.37	0.18	2.41
TMSZ	2.39	0.17	2.26
LANL1DZ	2.52	0.35	1.90
LANL1MB	2.57	0.28	1.61
LANL1(2s2p2d)/[1s1p1d]	2.39	0.88	12.68
ECMB	2.46	0.43	1.72
ECPB	2.42	0.50	2.25

3.2. Au-BDT-Au Complex. Since it has been demonstrated theoretically that the Au−S bond at the interface is strongly localized,[22] the simplest complex consisting of a BDT molecule with one gold atom on its each side is used to represent the gold electrode−BDT−gold electrode junction. As shown in Table 2, the optimized Au−S bond length using the LANL2DZ basis set for gold atoms is 2.35 Å, and bonding with gold atoms results in a charge transfer of ∼0.18 electron of charge from every gold atom to the BDT molecule, which is in good agreement with other theoretical results.[22] The binding energy (BE) is calculated to be 2.62 eV. Compared with calculated results of LANL2DZ, the Au−S bond length optimized using the TMDZ basis set is only 0.02 Å larger, the charge transfer is the same, and the binding energy is 0.21 eV smaller. The numerical accuracy of TMDZ is comparable to that of LANL2MB, which is the best one among all 11-electron ECP basis sets. The performance of TMSZ is a little inferior to that of TMDZ, but much better than that of LANL1DZ and LANL1MB. The Au−S bond length given by the LANL1DZ and LANL1MB basis sets is about 0.2 Å larger than that of LANL2DZ, and the binding energy calculated by them is about 1.0 eV smaller than that of LANL2DZ. Hence, TMSZ can be used when substantial computational resources are needed. Though the Au−S bond length calculated using the LANL1(2s2p2d)/[1s1p1d] basis set is close to that of LANL2DZ, both the charge transfer and the binding energy are too large. The charge transfer of 0.88 electron of charge is unbelievable, because the Pauling's electronegativity of the Au atom (2.54)

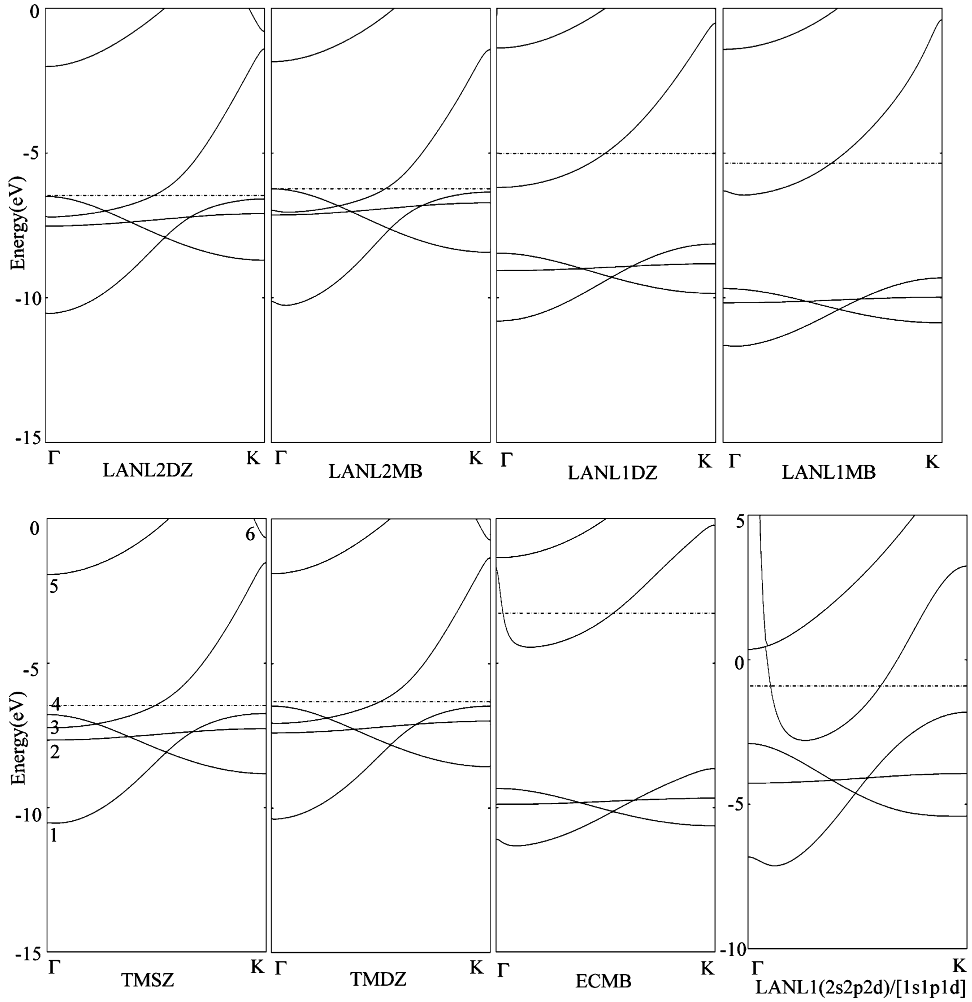

Figure 1. Band structures of an infinite 1D monatomic chain of gold.

TABLE 3: Comparison of Orbital Character of the Au−S Bond in the Optimized Au-BDT-Au Complex

	% s character		% p character		% d character	
	Au	S	Au	S	Au	S
SDD	86.96	3.44	0.31	96.35	12.73	0.20
LANL2DZ	87.20	3.55	0.16	96.24	12.64	0.21
LANL2MB	84.92	3.34	0.36	96.44	14.72	0.21
TMDZ	88.29	3.12	0.15	96.72	11.56	0.16
TMSZ	89.54	2.83	0.18	97.02	10.28	0.15
LANL1DZ	97.60	1.86	0.11	98.05	2.29	0.09
LANL1MB	98.02	1.61	0.34	98.31	1.64	0.09
LANL1(2s2p2d)/[1s1p1d]						
ECMB	94.08	2.32	4.81	97.55	1.11	0.12
ECPB	98.30	1.89	0.17	98.03	1.52	0.08

is almost the same as that of sulfur (2.58). The reason for this large error will be clearer in the following bonding nature analysis. The Au−S bond length and the binding energy calculated using the ECPB basis set is comparable to those of TMSZ, better than the performance of LANL1DZ; however, the ECMB basis set is not better than the LANL1DZ and LANL1MB basis sets. It should be noted that the number of basis functions of the ECPB basis set is 32, much more than that of the TMSZ basis set that includes only 9 basis functions, which indicates that basis sets with the TM ECP can obtain good results at a small price of computational effort.

The NBO analysis of the Au−S bond further corroborates that basis sets with the TM ECP are much superior to those with the LANL1 and EC ECPs dealing with the interaction between small gold clusters and organic molecules, as illustrated in Table 3. For the Au−S bond calculated using the LANL2DZ, LANL2MB, TMDZ, and TMSZ basis sets, the d-orbital contribution is roughly 10%, which correctly describes the hybridization of the 6s and 5d orbitals of Au due to the effect of relativistic corrections; however, the d-orbital contribution calculated using the LANL1DZ, LANL1MB, ECPB, and ECMB basis sets is only ∼1−2%, which is an inevitable result because the 5d orbital energy of an Au atom given by them is much lower than the 6s orbital energy. Though the description of the Au−S bond given by the LANL1DZ, LANL1MB, ECPB, and ECMB basis sets is still qualitatively correct, reflecting the partially ionic character of the covalent Au−S bond, the NBO analysis of the Au−S bond given by the LANL1(2s2p2d)/[1s1p1d] basis set is totally wrong, in which one electron belonging to an Au atom transfers to its neighboring S atom, forming a lonely electron pair with another unpaired electron of that S atom. This occurrence is completely due to the

TABLE 4: Comparison of Interatomic Distance of an Infinite 1D Gold Chain Optimized Using Different ECP Basis Sets

ECP basis	d_{NN} (Å)	ECP basis	d_{NN} (Å)
LANL2DZ	2.70	TMDZ	2.72
LANL2MB	2.72	TMSZ	2.73
LANL1DZ	2.83	ECMB	2.84
LANL1MB	2.87	LANL1(2s2p2d)/[1s1p1d]	2.51

incorrectly high 6s and 6p orbital energies of an Au atom given by the LANL1(2s2p2d)/[1s1p1d] basis set, which is also responsible for the unbelievably large charge transfer.

3.3. 1D Monatomic Gold Chain. The 1D monatomic gold chain is the simplest periodic structure of gold that has been studied extensively.[44−48] The interatomic distance is optimized using the BLYP functional with all ECP basis sets for gold; data are listed in Table 4. The nearest-neighboring distance (d_{NN}) calculated using the LANL2DZ basis set is 2.70 Å, only 0.09 Å larger than that of the SR calculation carried out using the all-electron full-potential linearized augmented plane wave (FPLAPW) method.[48] The performance of the TMDZ and TMSZ basis sets is as good as that of the LANL2MB basis set. However, the d_{NN} values calculated using LANL1DZ, LANL1MB, and ECMB are quite large, especially the LANL1MB basis set gives a d_{NN} value almost 0.2 Å larger than that given by the LANL2DZ basis, indicating that correlation effects are poorly represented by the LANL1 and EC ECPs.

Figures 1 and 2 show the band structure, density of states (DOS), and partial density of states (pDOS) of the 1D gold chain. The decomposition method of DOS is according to Hoffman.[49] When gold atoms form a 1D chain, discrete atomic levels will be broadened into continuous energy bands. Due to the small energy difference of 5d and 6s atomic orbitals, the s-band and d-band will be hybridized, which is described correctly by the LANL2DZ, LANL2MB, TMDZ, and TMSZ basis sets. The band structure and DOS calculated using the LANL2 ECP basis sets are consistent with the calculation results of the SR FPLAPW method,[48] which are almost the same as those obtained with the TM ECP basis sets, except for the position of the Fermi level.

In the band structures calculated using the LANL1DZ, LANL1MB, and ECMB basis sets, the 5d band and the 6s band are completely decoupled from each other, resulting in an s−d band gap of 1.4−3.5 eV. This still originates from the large energy difference between the 5d atomic states and the 6s atomic state of an Au atom calculated using these basis sets, and the broadening of energy levels during the formation of a 1D gold chain is not large enough to make the 5d and 6s bands overlap each other. The calculated Fermi level is completely located in the 6s band, as shown in Figure 2. If these basis sets are used in the calculation on the conductance of a gold chain at equilibrium,[10] there will be a certain energy range, roughly 1.5 eV below the Fermi level, in which the transmission coefficient is zero due to the wrong separation of the 5d and 6s bands, though the correct conclusion still can be drawn that the transmission coefficient at the Fermi level is unity.

Seen from the DOS and pDOS calculated using the LANL1-(2s2p2d)/[1s1p1d] basis, the DOS below the Fermi level is continuous, no apparent gap emerging. However, there is no

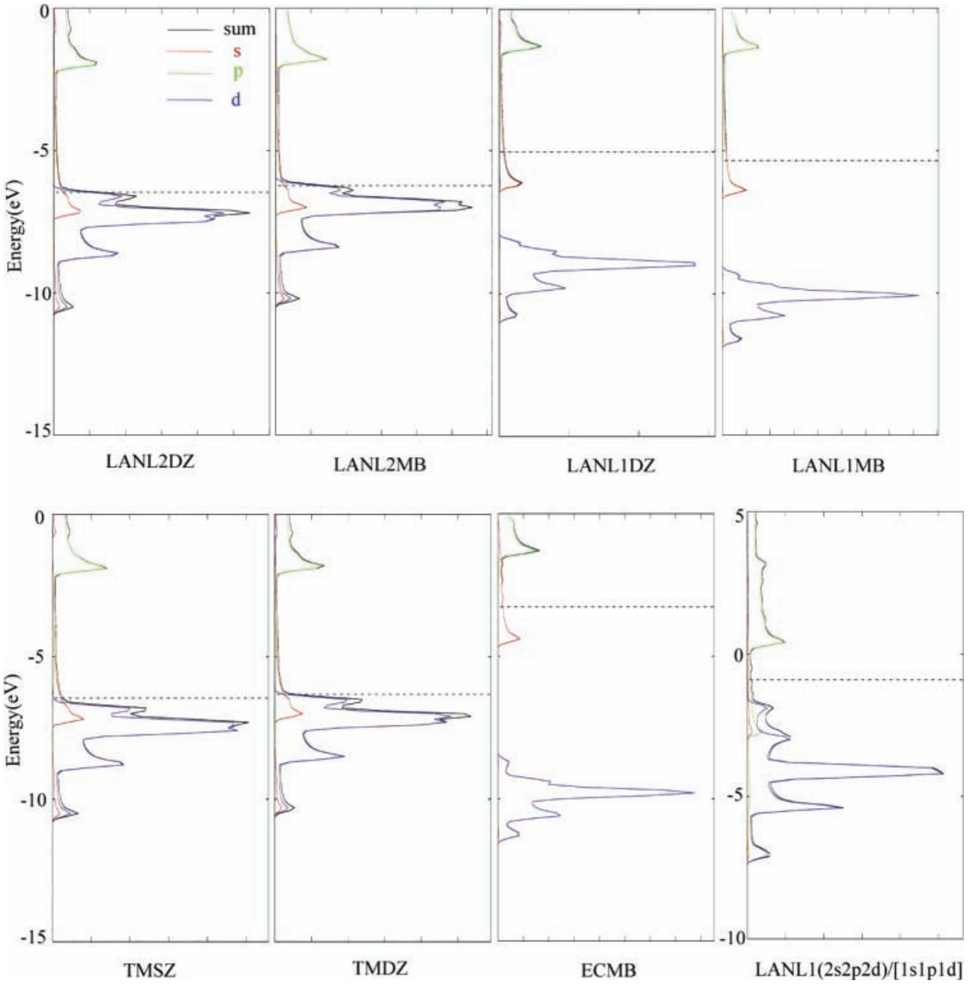

Figure 2. DOS and pDOS of an infinite 1D monatomic chain of gold.

s-state near the Fermi level, the 6s-band is located about 60 eV above the 5d-bands, which also results from the calculated energy of the 6s state being higher than that of the 5d states of an isolated gold atom. It is the 6p states that couple with the 5d states near the Fermi level.

Hence, TM is the only one with small basis sets among these three 11-electron ECPs that can give a good description about the electronic structure of a 1D gold chain. The number of bands crossing the Fermi level determines the number of conduction channels so that we examine in detail the band structure of 1D Au calculated using the TMSZ basis. Nine energy bands are labeled in an ascending sequence according to their values at the Γ point. Three bands among them are 2-fold degenerate, which are labeled as 2, 4, and 5. Band 5 is composed of $6p_x$ and $6p_y$ states. Band 2 is composed of $5d_{x^2-y^2}$ and $5d_{xy}$ states, the bandwidth of which is the smallest. Band 4 is composed of $5d_{xz}$ and $5d_{yz}$ states, and it approaches the Fermi level at the Γ point, only 0.32 eV below. Due to their symmetry, they cannot hybridize with other states. The magnetic number of the $5d_{z^2}$, 6s, and $6p_z$ atomic states is the same ($m = 0$), so that these states can hybridize when their energy values are close to each other. Band 1 has mainly d character, near the Γ point it has a mixture of 6s and $5d_{z^2}$ states (∼1:4), leading to some s states much below the Fermi level in the pDOS diagram; from the Γ point to the K point, the $5d_{z^2}$ state dominates this band. Band 3 is apparently an s-like band, at the Γ point it has a mixture of 6s and $5d_{z^2}$ states (∼3:1); from the Γ point to the K point, the proportion of the $5d_{z^2}$ state decreases, and the proportion of the $6p_z$ state increases, reaching almost 98% at the K point. Therefore, only band 3 intersects the Fermi level, implying that there is only one conductance channel. This is in contrast to fully relativistic (FR) and SR FPLAPW calculation results,[48] which state that there are three and two conductance channels, respectively. Experimentally, the conductance of suspended short monatomic chains of Au has been found to be close to unit conductance quantum G_0.[46] Hence, further examinations into both measurements and simulations are necessary, especially the nearest-neighboring distance d_{NN}, on which the position of the Fermi level sensitively depends. Decreasing the d_{NN} will enhance the interaction between d electrons of the nearest neighbors, which pushes the d bands to higher energies with the top of the d band reaching or intersecting the Fermi level.

4. Conclusion

Our DFT calculations on the neutral Au atom in the ground state, the Au-BDT-Au complex, and the 1D monatomic gold chain demonstrate that the performance of DFT-derived 11-electron ECP TMDZ and TMSZ basis sets in treating extended molecules and periodic structures of gold is better than that of basis sets derived for use with HF-based LANL1 and EC ECPs. Though this conclusion is drawn using the special BLYP exchange-correlation functional, the TM ECP basis set is actually very robust. For these three testing models, other popular functionals such as BPW91, PBEPBE, B3LYP, and B3PW91 combining with the TMSZ basis set all give correct results, very similar to the above ones given by the BLYP functional; details are given in the Supporting Information. Hence, the TM ECP and corresponding basis sets of gold are recommended in theoretical calculations on electrical properties of gold−molecule−gold junctions with the DFT-based Green's function method employing a finite analytic basis of local orbitals.

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Supporting Information Available: Detailed results of a neutral Au atom in ground state, the Au-BDT-Au complex, and the 1D monatomic gold chain calculated using BPW91, PBEPBE, B3LYP, and B3PW91 functionals. This material is available free of charge via the Internet at http://pubs.acs.org.

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