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Quantum stability and magic lengths of metal atom wires

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Metal atom wires represent an important class of nanomaterials in the development of future electronic devices and other functional applications. Using first-principles calculations within density functional theory, we carry out a systematic study of the quantum stability of freestanding atom wires consisting of prototypical metal elements with s-, sp-, and sd-valence electrons. We explore how the quantum mechanically confined motion and local bonding of the valence electrons in these different wire systems can dictate their overall structural stability and find that the formation energy of essentially all the wires oscillates with respect to their length measured by the number n of atoms contained in the wires, establishing the existence of highly preferred (or magic) lengths. Furthermore, different wire classes exhibit distinctively different oscillatory characteristics and quantum stabilities. Alkali metal wires possessing an unpaired s valence electron per atom exhibit simple damped even-odd oscillations. In contrast, Al and Ga wires containing three s^2p^1 valence electrons per atom generally display much larger and undamped even-odd energy oscillations due to stronger local bonding of the p orbitals. Among the noble metals, the s-dominant Ag wires behave similarly to the linear alkali metal wires, while Au and Pt wires distinctly prefer to be structurally zigzagged due to strong relativistic effects. These findings are discussed in connection with existing experiments and should also be instrumental in future experimental realization of different metal atom wires in freestanding or supported environments with desirable functionalities.

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I. INTRODUCTION

Metal atom wires have been extensively studied as prototypical one-dimensional (1D) systems that may exhibit exotic physical properties drastically different from their bulk counterparts, such as quantized conductance [1,2], end states [3–5], charge/spin density waves [6], and potential non-Fermi liquid behavior [7–9]. Efforts on such 1D or quasi-1D systems have been focused primarily on two categories, those that are freestanding or extended between two contacts [1,2,7,10–12], and those supported on different substrates [3,4,6,8], each system category also possessing its own challenges and opportunities in revealing new physical processes and concepts.

In exploiting various emergent properties of different atom wires, one particularly important aspect is the underlying physical factors determining their structural stabilities formed under diverse conditions using different fabrication approaches. For example, metal atom wires consisting of different elements have been fabricated using mechanical break junctions (MBJs) [2,7,10,11,13], while supported atom wires are typically fabricated through self-assembly processes of deposited atoms on highly anisotropic substrates or stepped surfaces [8,14–16]. These freestanding or supported atom wires have been shown to exhibit length-dependent electrical [2], electronic [3–5], optical [17,18], and magnetic [6,19–23] properties that are intimately connected to their precise atomic structures. It is therefore of substantial importance to reveal the dominant driving forces in the formation of atom wires, a prerequisite for gaining precise tuning of their structures and related functionality optimizations.

In this paper, we use first-principles approaches within density functional theory (DFT) and prototypical examples to explore systematically how the interplay between quantum mechanically confined motion and local bonding of valence electrons can dictate the overall structural stability of different classes of metal atom wires with increasing wire length. Here, by "quantum mechanically confined motion" we mean that the electrons are delocalized enough to fill the existence of the two boundaries or the end points, while by "local bonding of valence electrons" we stress more on the local nature of electron motion. The former is mainly for the s electrons, while the latter is mainly for the d electrons, with the p electrons likely lying in between. The potential importance of such quantum effects in the formation of metal atom wires has not been distinctively recognized, especially for supported wires, because these intrinsic effects cannot be readily separated from other extrinsic factors (e.g., strain or charge transfer effects). We find that the formation energy of essentially all the wires oscillates with respect to their length measured by the number n of atoms contained in the wires, establishing the existence of highly preferred (or magic) lengths. Furthermore, different wire classes exhibit distinctively different oscillatory characteristics. Alkali metal wires possessing an unpaired s electron per atom exhibit simple damped even-odd oscillations. In contrast, Al and Ga wires containing three s^2p^1 valence electrons per atom generally display much larger and undamped even-odd energy oscillations, due to stronger local bonding of the p orbitals. As a third class of elements, noble metal wires show intriguing and contrasting behaviors. Qualitatively, the s-dominant Ag wires behave

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similarly to the linear alkali metal wires, but quantitatively the oscillation magnitudes are much larger. In contrast, Au and Pt wires prefer to be structurally zigzagged due to strong relativistic effects, respectively with presence or absence of even-odd oscillations in the formation energy because of odd or even number of valence electrons per atom. These findings represent a significant step forward towards a more complete understanding of the underlying physical factors determining the structural, electrical, and magnetic properties of metal atom wires in diverse environments. In a broader perspective, the present study of 1D metal wires effectively complements our understanding of quantum stability in other low-dimensional metal systems, where magic sizes or magic thicknesses have been established in 0D clusters [24–26] or ultrathin (or quasi-2D) metal films [27–30], respectively.

It should be emphasized that, whereas earlier studies of atom wires suspended between MBJs or supported on different substrates dealt with physically more realistic environments, such studies cannot readily differentiate the intrinsic quantum size effects from extrinsic factors such as strain or charge transfer. To best assess the possible existence of the intrinsic quantum stability, idealized models treating freestanding atom wires are actually preferred, so as to separate such contributions from other extrinsic effects. Such new insight, obtained here from freestanding atom wires, should serve as the basis for a more complete understanding of atom wires under diverse physically more realistic conditions.

The paper is organized as follows. In Sec. II, we briefly describe the first-principles method used and the definitions of formation energy and structural stability as measured by the second difference of the formation energy. In Sec. III, we present the energetics of freestanding metal atom wires consisting of prototypical elements with *s*-, *sp*-, and *sd*-valence electrons, and show how the quantum mechanically confined motion and local bonding of the valence electrons in these systems can dictate their overall structural stability. In Sec. IV, we make closer connections with experimental aspects and also discuss the influence of the quantum stability of the atom wires on their transport and other properties. Finally, we conclude in Sec. V.

II. METHODS

In our studies, the total-energy and force calculations were performed using the projector-augmented wave method [31] implemented in the Vienna *ab initio* simulation package (VASP) [32,33]. For the exchange-correlation functional, we used the generalized gradient approximation of Perdew, Burke, and Ernzerhof [34]. A plane-wave basis set was used with an energy cutoff of 300 eV, and various metal atom wires of finite lengths were simulated using $15 \times 15 \times 60\ \text{Å}^3$ or larger unit cells, with larger than 12 Å of vacuum along the wire direction. For infinite wires, both one-atom and two-atom unit cells were adopted, with $1 \times 1 \times 128$ and $1 \times 1 \times 64$ *k* points used to sample the 1D Brillouin zone, respectively, leading to converged bond lengths. For finite wires, the initial configuration of an n-atom wire was set according to the configuration of an $(n-1)$-atom wire plus one additional atom, and the structures were fully relaxed by the conjugate gradient method until all the residual force components were less than 0.01 eV/Å. The relativistic effects were at the scalar-relativistic level.

The formation energy of a wire containing n atoms is defined by $E(n) = E_t(n) - E_t(n-1) - E_{\text{atom}}$, where $E_t(n)$ is the total energy of the wire containing n atoms and E_{atom} is the total energy of an isolated atom. Generally, a negative value of the formation energy for a given wire length means that the wire is stable. Following this simple definition, all the wires considered in the present study are stable. In this paper, we place more emphasis on the relative stability of the wires, defined by the thermodynamic stability, which can be expressed by the second difference of the formation energy, $\Delta^2 E(n)/\Delta n^2 = E_t(n+1) - 3E_t(n) + 3E_t(n-1) - E_t(n-2)$. If $\Delta^2 E(n)/\Delta n^2 > 0$, the wire is thermodynamically stable against small scale variations in the wire length, otherwise it is thermodynamically unstable [28,30].

III. RESULTS

A. An overview on the atomic structures of different wires

We first discuss the preferred atomic structures of different wires, starting with infinite wires as reference systems. For such infinite wires, we have examined periodic lattice distortions due to Peierls instability. We limit ourselves to linear and nearly-linear zigzagged configurations, excluding clusterlike compact structures. For all the linear structures considered, it is found that the Peierls effect is more pronounced for Na and K, giving rise to bond length alternations of 0.024 Å and 0.018 Å, respectively; in contrast, negligible bond length alternations (within 0.001 Å) are present for the other systems. A linear configuration is the ground state for the alkali metal wires, but other classes of metal atom wires with hybridized valence electrons typically prefer to be zigzagged. In particular, the Au and Pt wires strongly prefer the zigzag configurations, by 0.22 and 0.31 eV/atom than the linear structures, with the bond angles of ∼133° and ∼129°, respectively. The underlying reason is the strong relativistic effects in these latter two systems, as discussed later.

For wires of finite lengths, the leading structural feature is consistently the even-odd oscillations in the bond length, as shown in Fig. 1. Both Na and Ag wires prefer linear configurations. Whereas wires containing even numbers of atoms display simple and complete even-odd oscillations in bond length, wires containing odd numbers of atoms exhibit much weaker even-odd oscillations with a phase change at the center of the wires. Au wires prefer to be structurally zigzagged, and the oscillations in bond length are similar to those of Na and Ag wires, but with much smaller magnitudes (less than 0.05 Å). Al and Ga wires prefer linear or nearly linear configurations, and show less regular oscillatory behaviors in bond length. All these bond length alternations are significantly larger than those of the corresponding infinite wires.

B. Alkali metal wires with an unpaired *s* electron per atom

The first class of systems consists of alkali metal wires, with Na as a detailed example. Since Na has only one unpaired *s* valence electron per atom, the stability of Na wires is expected to be enhanced whenever all the valence electrons pair up. Indeed, the formation energy $E(n)$, defined

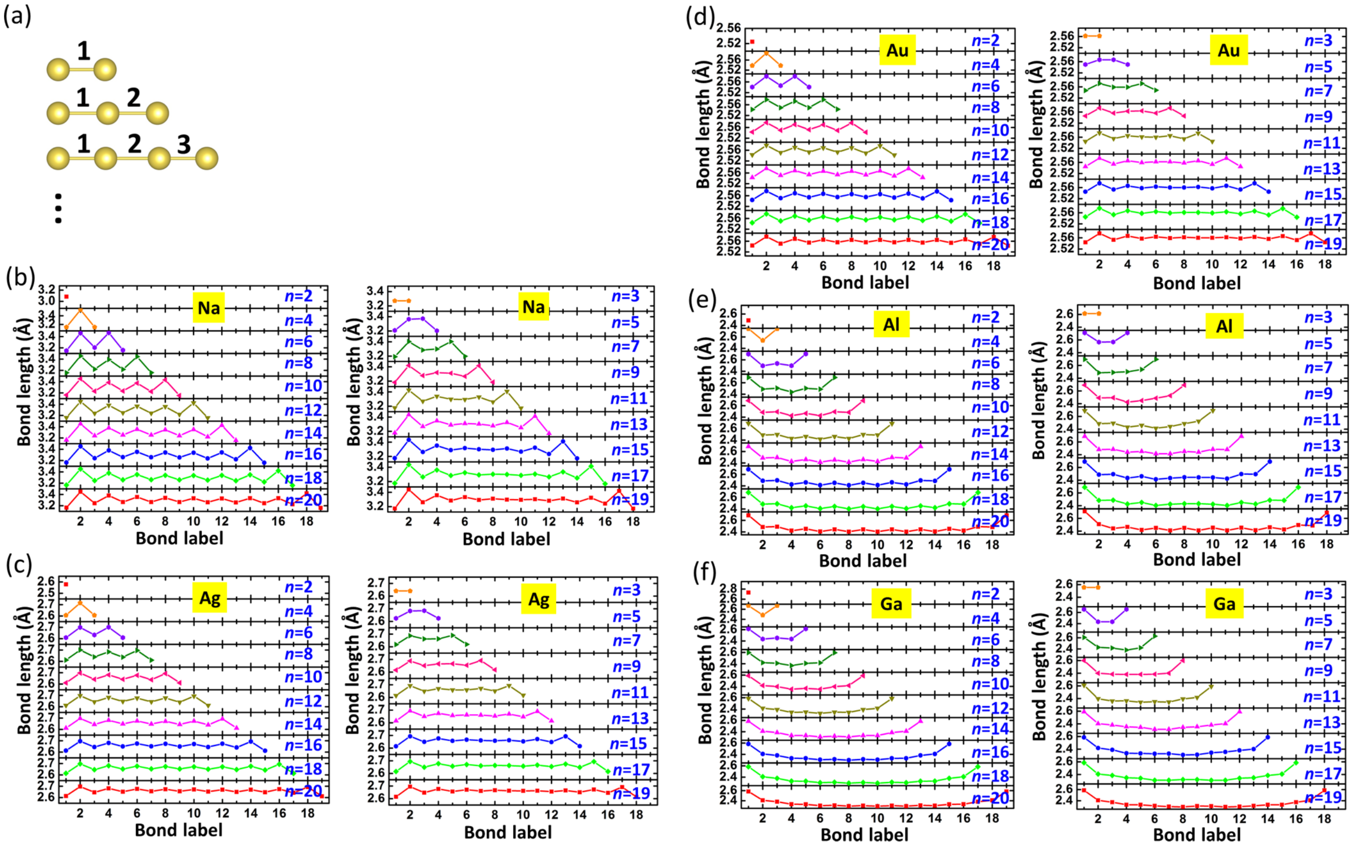

FIG. 1. (a) Labeling of the bonds in different wires. Optimized bond lengths of (b) linear Na, (c) linear Ag, (d) zigzagged Au, (e) linear Al, and (f) linear Ga wires with different wire lengths n of even numbers (right side) and odd numbers (left side) of atoms.

as the energy gain from the cohesion of one additional atom, shows even-odd oscillations with respect to the wire length [Fig. 2(b)]. Such oscillations are damped in magnitude as the wire length increases, caused by the weakening quantum confinement effects. Nonetheless, the energy differences are still considerable even up to wire lengths as long as $n = 20$. As a secondary effect, we note that all the DFT calculations have been performed with spin polarization, showing that antiferromagnetic or ferromagnetic ordering can further lower the total energies of odd-numbered Na wires, but without altering the overall nature of the even-odd oscillations. The detailed comparison is given by Figs. 2(a) and 2(b). The presence of (anti-)ferromagnetic orders in such 1D but finite systems is qualitatively consistent with previous experimental observations in related systems [19,22].

Here we also introduce the stability of a wire containing n atoms, determined by the second difference of the formation energy, $\Delta^2 E(n)/\Delta n^2$. As shown in Figs. 2(a) and 2(b), Na wires with even numbers of atoms have positive $\Delta^2 E(n)/\Delta n^2$, and are therefore stable. Moreover, K atom wires show similar stabilities, as shown in Fig. 2(d). We also observe more regular even-odd oscillations in the bond lengths for even-numbered atom wires, while such oscillations in the bond lengths are either absent or more irregular for odd-numbered atom wires.

C. Poor metal wires with three s^2p^1 valence electrons per atom

As the second class of systems, we study the stability of Al and Ga wires with three s^2p^1 valence electrons per atom. Here the two s valence electrons fill the sp_z hybridized band, which is lower than the partially filled p_x/p_y bands [see Figs. 3(c) and 3(d)]. Accordingly, the unpaired p electron plays a more significant role in determining the stability of the Al and Ga wires, resulting in a simple pairing sequence, but stronger than the cases of unpaired s electrons associated with the alkali metal wires. Indeed, as shown in Figs. 3(a) and 3(b), the calculated formation energies of the Al and Ga wires also show even-odd oscillations, which are much stronger in magnitude, and essentially undamped because of the more dominant localized bonding. For shorter wires with $n \leqslant 5$, the oscillatory nature is less regular, caused by comparable effects of quantum confinement and local bonding.

As shown in Figs. 1(e) and 1(f), we observe weaker but systematic even-odd oscillations in the bond length near the central parts of the wires, irrespective of their total lengths. A more distinct feature is the longer bond lengths at both ends of a given wire than those of the central parts. This feature contrasts those for other systems considered, which show contractions at both ends of the wires. The underlying physical reason could be tied to the different spillings of valence electrons at the wire ends, similar to lattice expansions or contractions at the surfaces of different metals [35,36].

D. Noble metal wires with *sd* valence electrons

Noble metal wires with sd valence electrons show intriguing and contrasting structural and stability behaviors both among themselves and in comparison with other classes of

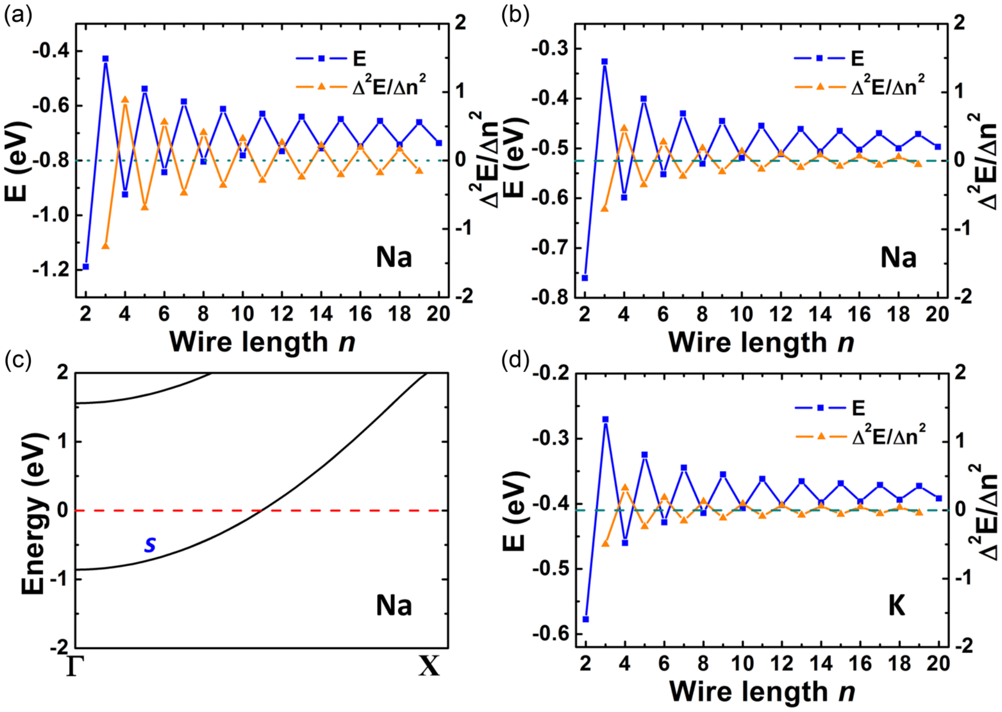

FIG. 2. Calculated formation energy E of freestanding Na wires as a function of the wire length n (a) without and (b) with spin polarization. The second difference $\Delta^2 E(n)/\Delta n^2$ of the formation energy is also given. (c) Calculated orbital-decomposed band structure of an infinitely long Na wire with spin polarization, as calculated using a one-atom unit cell. Here and also in Figs. 3, 4, and 5, the Fermi level is set to the energy zero (dashed red line). (d) Calculated formation energy E of freestanding K wires as a function of the wire length n with spin polarization.

elements. As the simplest example, we first note that Ag wires prefer to be linear, and display simple even-odd oscillations in the formation energy [Fig. 4(a)], similar to the cases of alkali metal wires. This is somewhat surprising at first sight, but is inherently tied to the fact that the highest occupied wire state (HOWS) predominantly originates from the unpaired *s* orbitals, while the occupied *d* bands are much lower in energy as shown in Fig. 4(c), rendering the systems to be *s* dominant.

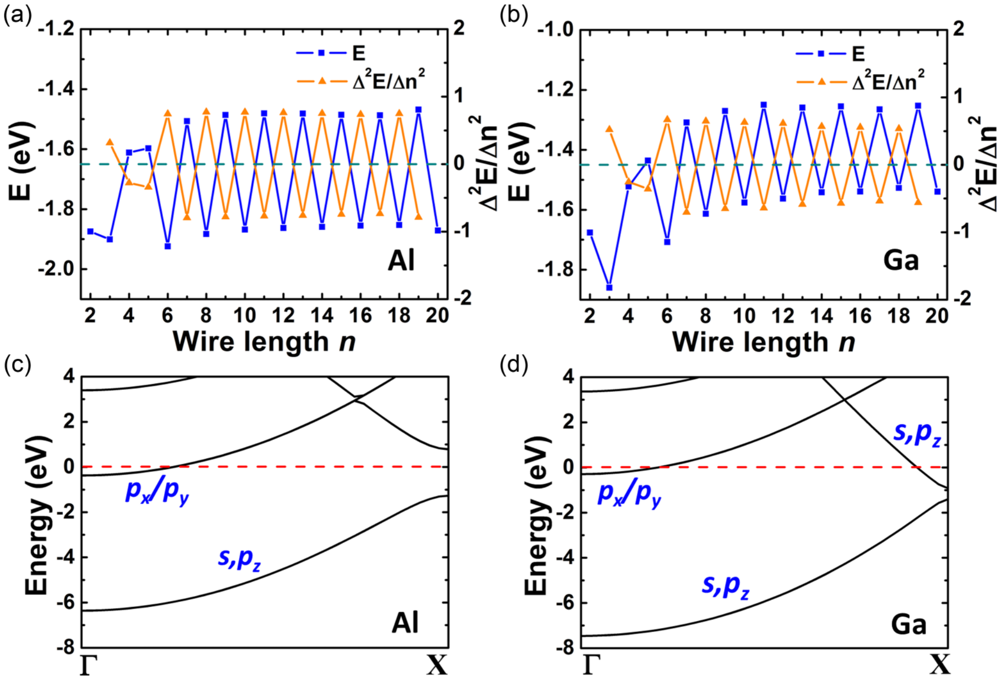

FIG. 3. Calculated formation energy E of freestanding (a) Al and (b) Ga wires as a function of the wire length n with spin polarization. Calculated orbital-decomposed band structures of infinitely long (c) Al and (d) Ga wires, as calculated using one-atom unit cells.

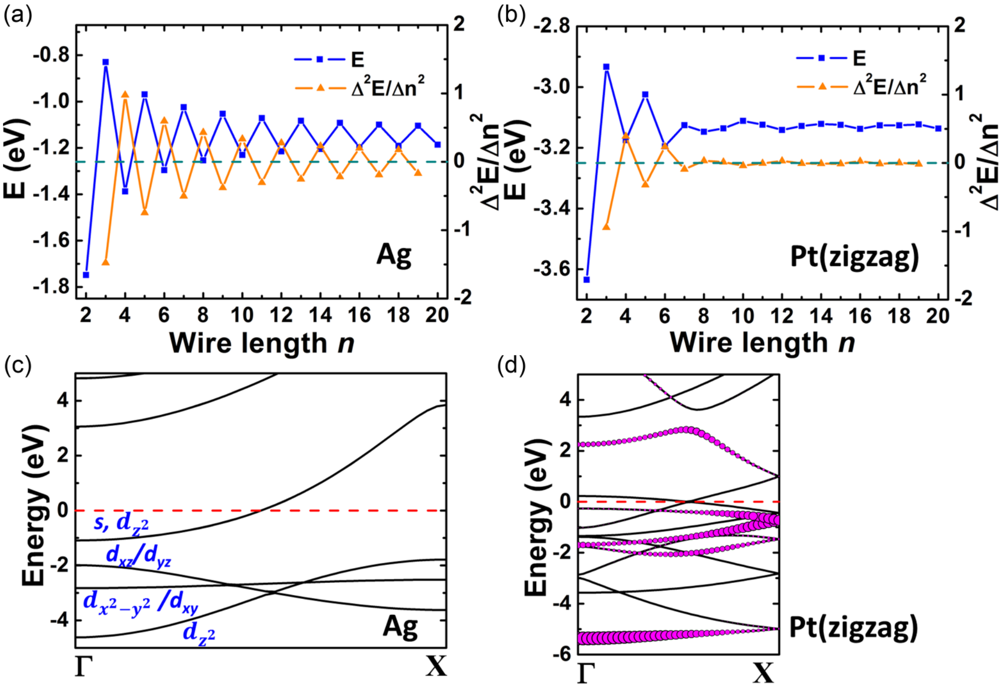

FIG. 4. Calculated formation energy E of freestanding (a) linear Ag and (b) zigzagged Pt wires as a function of the wire length n with spin polarization. Calculated orbital-decomposed band structures of (c) an infinitely long linear Ag wire calculated using a one-atom unit cell and (d) an infinitely long zigzagged Pt wire using a two-atom unit cell. The magnitudes of the contributions from the s orbitals are indicated by the sizes of the pink solid spheres in (d).

As the second example of the noble metals, Au wires have considerable hybridization of the highest occupied s and lower d bands, arising from the strong relativistic contraction of the 6s orbital [37,38], as shown in Figs. 5(c) and 5(d). As a consequence, the HOWS is deformed from the isotropic 6s orbital, breaking the rotational symmetry with respect to

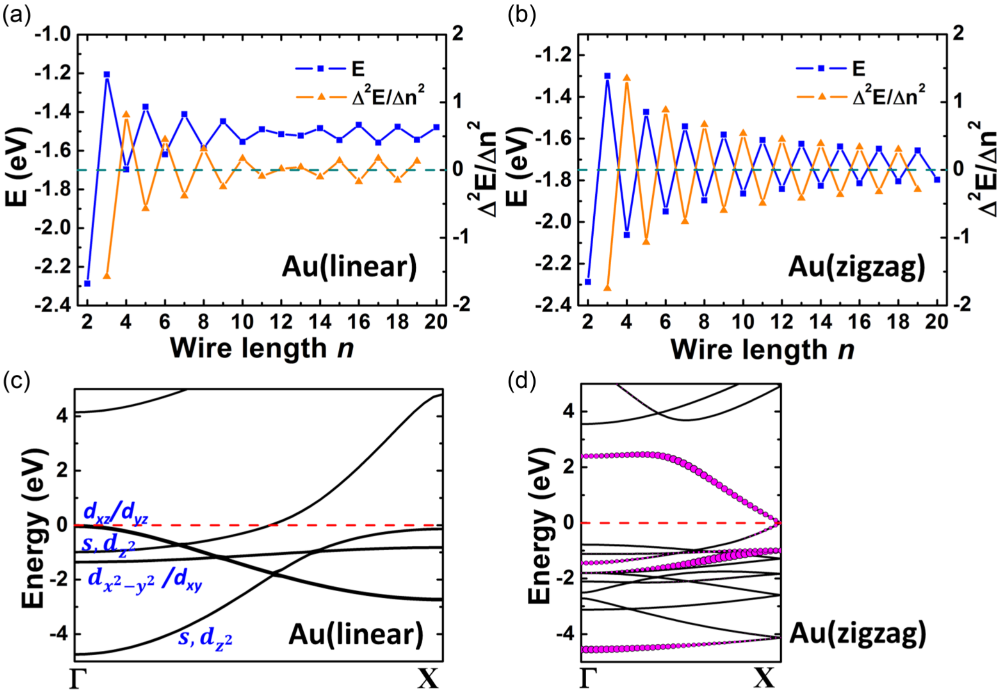

FIG. 5. Calculated formation energy E of freestanding (a) linear and (b) zigzagged Au wires as a function of the wire length n with spin polarization. Calculated orbital-decomposed band structures of (c) an infinitely long linear Au wire calculated using a one-atom unit cell and (d) an infinitely long zigzagged Au wire using a two-atom unit cell. The magnitudes of the contributions from the s orbitals are indicated by the sizes of the pink solid spheres in (d).

the wire axis and favoring bond formation with a preferred angle, as already mentioned for the infinitely long Au wires and also emphasized in previous studies [39]. For the finite Au wires, zigzagged configurations are also energetically lower than the corresponding linear ones. Furthermore, the even-odd oscillations in the formation energy are preserved because of the dominance of the *s* electrons [Figs. 5(a) and 5(b)]. For Au wires, we have checked the effects of different onsite Coulomb repulsions within the (GGA+U) scheme, and found the effects of onsite repulsions to be secondary to the relativistic effects that favor zigzag wires. Here we further note that qualitatively similar (e.g., corrugated or helical) structural features have been identified in other low-dimensional Au structures, including clusters [37,40], nanowires [41], and surfaces [42], and these intriguing features may all be inherently connected to the strong relativistic effects in Au [38].

As the third example of the noble metals, Pt is nearly as heavy as Au and is therefore expected to show strong relativistic effects as well. Indeed, we find that zigzagged Pt wires are energetically more stable than the corresponding linear ones, similar to a previous report for suspended Pt wires [43]. Such zigzagged Pt wires, however, exhibit more complex oscillations in their formation energy beyond the simple even-odd nature [see Fig. 4(b)], because each Pt atom contains an even number of valence electrons (one *s* and nine *d* electrons). This last observation explains why the formation energy exhibits much weaker variations when the wire length exceeds a crossover value of a few atoms.

IV. DISCUSSIONS

Before closing, we make closer connections with experimental aspects, including how to observe the quantum stability of atom wires as revealed here, and different manifestations of the quantum stability. As a more realistic example, we note that metal atom wires supported on some specific substrates involve some extrinsic effects such as strain or charge transfer, due to hybridization between the atomic orbitals of the wires and surface states. Despite the existence of such extrinsic effects, the intrinsic effects can be observed experimentally by elegant tuning of the interaction between the wires and the substrates. For example, if the coupling between the atom wires and the substrates is via van der Waals interaction, both the strain and charge transfer effects would be minimal, thereby rendering the quantum stability more likelihood to be the dominant factors. Since the noble metal wires of Ag and Au display much stronger oscillatory behaviors in the formation energy than the other considered systems, we expect their quantum stabilities are more readily observable experimentally, for example on properly selected substrates. In this regard, we note that several recent studies of Au and Ir wires grown on different semiconductor substrates already revealed strong preferences of certain wire lengths, and the underlying mechanism has been suggested to be due to quantum size effects [44,45]. We also observe that in a recent experimental study of In wires grown on the Si(100) surface, certain preferred wire lengths and size oscillations are distinctly visible, though not very well defined [see Fig. 3 in Ref. [46]]. Furthermore, given the undamped nature of the formation energy oscillations for the Al and Ga wires, and the distinctly zigzagged geometries preferred by the Au and Pt wires, we expect convincing future experimental validations of those predictions.

Based on the present study showing the potential importance of quantum size effects in defining the overall stability and the dominant growth modes of such atom wires, better controlled experiments can be performed to fully exploit the influence of quantum stability on the formation mechanisms of the respective low-dimensional materials. In particular, a reasonably high growth temperature is typically needed, in order for the constituent adatoms to have sufficient mobility to explore the morphological phase diagram and potentially exhibit the quantum size effects as they form wires of different lengths, as demonstrated in a related study of the quantum size effects in the coarsening of ultrathin Pb islands on Si(111) at a given total Pb coverage [47]. We may also expect unusual growth kinetics of such 1D or quasi-1D wires, given the potential dominance or significant influence of the quantum stability as the wires grow.

In addition to the quantum stability of the atom wires discussed above, the changes in the wire lengths may also affect their conductivity and other properties. As depicted in Fig. 6, the gap between the HOWS and the lowest unoccupied wire state (LUWS) of a typical wire system shows the same even-odd oscillations as the formation energy, with more stable structures possessing larger HOWS-LUWS gaps, as commonly expected. A closer analysis reveals that these even-odd oscillations in the HOWS-LUWS gap size are directly correlated to the presence of the half-filled states arising from unpaired electrons. Such unpaired electrons, in

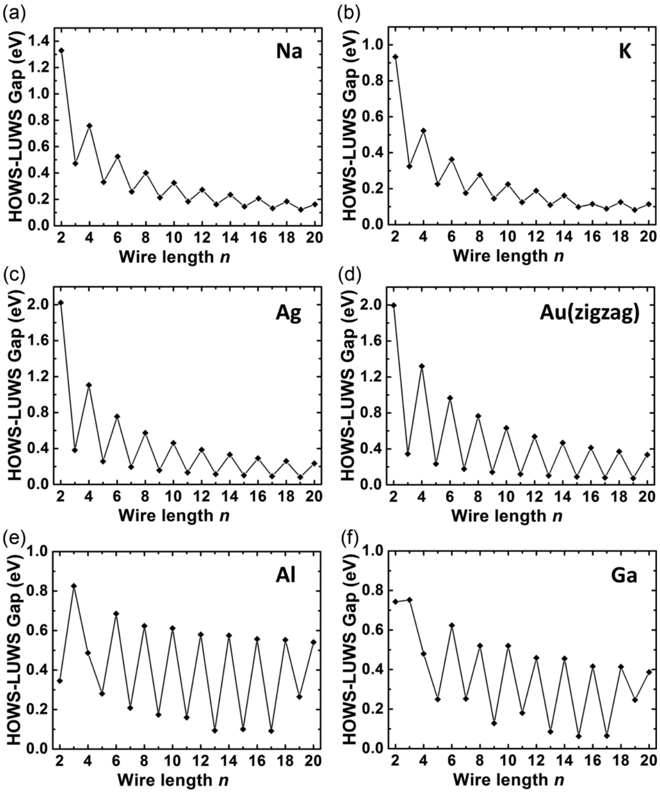

FIG. 6. Calculated energy gaps between the LUWS and HOWS as a function of the wire length *n* of six different elements.

turn, are more likely to hop from site to site, potentially resulting in similar oscillatory behaviors in the quantized conductance. Indeed, such oscillatory conductance has been frequently observed experimentally or theoretically in atom wires extended between two break junction contacts [2,48–54], in some cases with the additional complication of molecular adsorption onto the wires [55,56]. In this regard, we note that in Ref. [54] a 4-atom periodicity in the conductance is reported experimentally for Au wires adsorbed on Si(111), while in Fig. 6(d) the HOWS-LUWS gap exhibits 2-atom periodicity. This comparison does not necessarily imply a contradiction between the results, because the Au wires studied experimentally have a wire width of three (or four) atoms, while the Au wires considered in the present study are single-atom wires, and the increase in the wire width is likely to change the oscillation period of either the conductance or the HOWS-LUWS gap, or both. We also note that in Ref. [51], the Al atom wires considered are in the few-atom regime, which also displays apparent irregular variations in both the formation energy and HOWS-LUWS gap in the present study; the regular 2-atom oscillations in the stability or HOWS-LUWS gap are well defined only for longer wires. Furthermore, a recent scanning tunneling microscope (STM) study of the Ag/Ag(111) system revealed that the resonance peaks of the unoccupied states vary distinctively with the wire length, though no apparent oscillatory behavior is revealed, probably due to too strong wire-substrate interactions [57]. As a limiting example, a very recent experimental study also showed the importance of specific atomic configurations in the conductance of atomic junctions formed between an STM tip and a metal substrate [58]. We further expect that the quantum stability will influence the magnetic properties of such atom wires (especially those consisting of transition metal atoms) [59], a subject of importance to be more systematically explored in future studies.

V. CONCLUSIONS

In summary, we have performed a systematic study of quantum confinement and local bonding on the overall structural stability of various metal atom wires by means of first-principles calculations. We found that different wire classes exhibit different oscillatory behaviors in the formation energy, thereby defining different sets of highly preferred or magic wire lengths. We have also shown that the strong relativistic effects in heavy noble metals lead to zigzagged geometries of the wires. These strong predictions are not only helpful in gaining a deeper understanding of a line of existing experimental observations but also are expected to stimulate future research efforts on controlled fabrication of metal atom wires for optimal properties and quantum device applications.

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