First-principles calculations of equilibrium ground-state properties of Au and Ag

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The equilibrium ground-state properties of the noble metals Ag and Au are calculated from first principles, using norm-conserving pseudopotentials. We have obtained the cohesive energies, bulk moduli, and lattice constants of Ag and Au, which are in very good agreement with experiments. We have also examined the importance of the relativistic effects in governing the structural properties of Au.

I. INTRODUCTION

A comparison of silver $[\text{Kr}]4d^{10}5s^1$ and gold $[\text{Xe}]5d^{10}6s^1$ reveals at the same time some similarities and some striking differences. Although the $5d$ metals have, in general, bigger core radii than the $4d$ metals, the lattice constants of Au and Ag are almost identical. More importantly, all the low-index surfaces of Au exhibit reconstructions that are not seen in the respective Ag surfaces.¹⁻³ In this paper, we have used Hohenberg-Kohn-Sham local-density-functional theory to obtain the cohesive energies, bulk moduli, and lattice constants of bulk silver and gold. Calculations have been done before using different approaches,⁴⁻⁶ but the ground-state crystal structure for Au has not always been correctly predicted. We found that a large number of k points are required to obtain the correct ground-state crystal structure. The differences in the bulk and surface properties of Au and Ag are found to originate from relativistic effects which lower the position of the s -like electrons relative to the d bands. The rest of the paper is organized as follows: the pseudopotentials used in the calculations are described in Sec. II, the calculational procedures are described in Sec. III, the results are presented in Sec. IV, and the conclusion of the paper is in Sec. V.

II. PSEUDOPOTENTIAL

We have used in our calculations nonlocal ionic pseudopotentials generated using the norm-conserving scheme of Hamann, Schlüter, and Chiang.⁷ These angular-momentum-dependent pseudopotentials are constructed by constraining their pseudo-wave-functions to match the ground-state, all-electron, valence-electron wave functions exactly outside some "core radius," as well as reproducing the same atomic eigenvalues for the valence states.

Au is a heavier atom than Ag. One then expects relativistic effects to be more important in Au than in Ag. Relativity mostly affects the core electrons, especially electrons in s orbitals which have substantial amplitudes near the atom. The effect on the valence electronic structure is a lowering of the s -like bands relative to the d -like bands. In our calculations, this effect (the scalar-relativistic effect) is included by constructing our pseudo-

FIG. 1. (a) The angular-momentum-dependent pseudopotential for Ag. (b) The angular-momentum-dependent pseudopotential for nonrelativistic Au. (c) The angular momentum dependent (scalar-relativistic) pseudopotential for Au.

TABLE I. Eigenvalues and excitation energies of the pseudoatom for different configurations of scalar-relativistic Au. Values in parentheses denote the deviations from the corresponding all-electron results.

Configuration	<i>d</i>	Eigenvalues (Ry)		Excitation energy (Ry) (ΔE_{tot})
		<i>s</i>	<i>p</i>	
$5d^{10}6s^1$	−0.5267 (0.0023)	−0.4502 (0.0038)	−0.0728 (−0.0023)	0
$5d^96s^2$	−0.6803 (−0.0015)	−0.5126 (0.0055)	−0.0986 (−0.0014)	0.1210 (0.0040)
$5d^{10}6p^1$	−0.6750 (0.0053)	−0.5624 (0.0058)	−0.1549 (−0.0012)	0.3908 (−0.0062)
$5d^96s^16p^1$	−0.8248 (0.0001)	−0.6188 (0.0068)	−0.1748 (−0.0007)	0.5491 (−0.0041)
$5d^86s^26p^1$	−0.9889 (−0.0070)	−0.6782 (0.0076)	−0.1959 (0.0003)	0.8065 (0.0075)

potential by fitting to all-electron results obtained from solving the Dirac equation for the atom. The other relativistic effect, spin-orbit coupling, is not included in our calculations. In order to check the importance of the relativistic effects in Au, we have generated both a nonrelativistic and a scalar-relativistic pseudopotential for Au. The Ag, Au nonrelativistic, and Au scalar-relativistic pseudopotentials are shown in Fig. 1. This can be understood as an effect coming from the changes in core-orthogonality repulsion as relativity produces a shrinking in the orbitals of the core *s* electrons. To check the transferability of our pseudopotential, we compare the eigenvalues and excitation energies for various atomic configurations above the ground state obtained from the pseudopotentials with the corresponding all-electron values. The results are listed in Tables I–III. We see that the pseudopotential results reproduced the all-electron results with an error of less than 0.008 Ry for all excited configurations.

III. METHOD OF CALCULATION

The total energy of the crystal is calculated within the local-density-functional formalism⁸ using a mixed-basis approach.⁹ The total energy can be written as¹⁰

$$\begin{aligned}
 E_{\text{total}} = & \sum_{n,\mathbf{k}} f_{n\mathbf{k}} \epsilon_{n,\mathbf{k}} - \Omega_{\text{cell}} \sum_{\mathbf{G}} \rho(\mathbf{G}) V_{\text{sc}}(\mathbf{G}) \\
 & + \Omega_{\text{cell}} \frac{1}{2} \sum_{\mathbf{G} (\neq 0)} 8\pi |\rho(\mathbf{G})|^2 / |\mathbf{G}|^2 \\
 & + \Omega_{\text{cell}} \sum_{\mathbf{G}} \rho(\mathbf{G}) \epsilon_{\text{xc}}(\mathbf{G}) + \gamma_{\text{Ewald}} + \alpha_1 Z_v, \quad (1)
 \end{aligned}$$

where *n* and *k* are band and *k*-point indices, respectively, and the *G*'s are the reciprocal-lattice vectors. The first term is the sum of the occupied-band energy. In the second term the $V_{\text{sc}}(\mathbf{G})$'s are the Fourier components of the input screening potential for the self-consistent calculation and the $\rho(\mathbf{G})$'s are the Fourier components of the charge density. The difference of these two terms gives

TABLE II. Eigenvalues and excitation energies of the pseudoatom for different configurations of Ag. Values in parentheses denote the deviations from the corresponding all-electron results.

Configuration	<i>d</i>	Eigenvalues (Ry)		Excitation energy (Ry) (ΔE_{tot})
		<i>s</i>	<i>p</i>	
$4d^{10}5s^1$	−0.6029 (0.0003)	−0.3169 (0.0049)	−0.0700 (0.0002)	0
$4d^{10}5p^1$	−0.7340 (0.0034)	−0.4096 (0.0035)	−0.1385 (−0.0001)	0.2561 (−0.0043)
$4d^95s^2$	−0.8644 (0.0026)	−0.4085 (0.0067)	−0.1139 (0.0004)	0.3714 (0.0050)
$4d^95s^15p^1$	−0.9827 (−0.0059)	−0.4851 (0.0022)	−0.1728 (0.0024)	0.6729 (0.0035)

TABLE III. Eigenvalues and excitation energies of the pseudoatom for different configurations of nonrelativistic Au. Values in parentheses denote the deviations from the corresponding all-electron results.

Configuration	Eigenvalues (Ry)			Excitation energy (Ry) (ΔE_{tot})
	d	s	p	
$5d^{10}6s^1$	-0.6148 (0.0000)	-0.3315 (0.0002)		0
$5d^{10}6p^1$	-0.7376 (0.0005)	-0.4159 (0.0002)	-0.1417 (0.0001)	0.2643 (-0.0001)
$5d^96s^2$	-0.8362 (-0.0052)	-0.4095 (0.0019)	-0.1154 (0.0016)	0.3536 (0.0034)
$5d^96s^16p^1$	-0.9483 (-0.0062)	-0.4841 (0.0013)	-0.1731 (0.0013)	0.6558 (0.0032)
$d^{8.5}6s^{1.5}6p^{0.5}$	-1.5983 (-0.0069)	-0.9932 (0.0032)	-0.6087 (0.0039)	1.4773 (0.0052)
$5d^86s^{0.5}6p^{0.5}$	-2.3988 (0.0089)	-1.6136 (0.0040)	-1.1586 (0.0057)	3.1223 (0.0072)

the kinetic energy of the electrons and the interaction of the electrons with the ion cores through the pseudopotential. The third term corresponds to electron-electron repulsion, and the fourth term is the exchange-correlation energy of the electrons within the local-density approach (with the Hedin-Lundqvist¹¹ form for the exchange and correlation). γ_{Ewald} is the ion-ion Coulomb energy¹² and α_1 is given by

$$\alpha_1 = (1/\Omega_{\text{at}}) \int [U_{\text{ps}}^L(\mathbf{r}) + (2Z_v/r)] d\mathbf{r}, \quad (2)$$

where Ω_{at} is the atomic volume, and U_{ps} is the local part of the ionic pseudopotential, and Z_v is the effective charge of the ion core.

The localized character of the d electrons makes the expansion for the wave functions in plane waves uneconomical. In order to treat a system such as this, whose electronic wave functions contain both tightly bound atomiclike character as well as extended plane-wave-like character, an energy-independent basis set containing both plane waves and Bloch sums of localized orbitals were used to represent the electronic wave function. For Au, our basis set consists of plane waves with energy $(\mathbf{k} + \mathbf{G})^2$ up to certain E_{cut} , and a set of Gaussian local orbitals of the form

$$f_m(\mathbf{r}) = N r^2 \exp(-\gamma r^2) Y_{lm}(\mathbf{r}), \quad (3)$$

where N is the normalization constant, and l and m are the angular-momentum indices ($l=2$, i.e., d orbitals are used). The Gaussian exponents γ are chosen to optimize the energy of the system. We used $E_{\text{cut}} = 12$ Ry and $\gamma = 1.33$.

In the case of silver, due to the fact that the $4d$ states are more localized than the Au $5d$ states, we have used for the local orbital a numerical basis of the form

$$f'(r) = \begin{cases} B f(r) \{1 - \exp[-\alpha(r_c - r)^2]\}, & r \leq r_c \\ 0, & r > r_c \end{cases} \quad (4)$$

where $f(r)$ is a radial function closely related to the radial distribution of the atomic d wave function, B is a normalization constant, and α is determined variationally (see the Appendix). The advantage of using the numerical basis is twofold: it is more efficient, i.e., convergence can be achieved with less plane waves, and second, the "on-site" approximation⁹ becomes exact if r_c is smaller than the nearest-neighbor distance. For a value of $E_{\text{cut}} = 10.5$ Ry the optimal value of α is 0.7. To compare the two different basis sets, we have also included a calculation for the fcc structure of Ag using Gaussian orbitals, with a much larger value of E_{cut} (18 Ry) and a value of 2.03 for the Gaussian exponent γ . The results for the bulk modulus and the lattice constant are essentially the same for the two calculations. The only significant difference is a bigger cohesive energy when the numerical local orbitals are used, indicating that the numerical basis is better converged. In the case of Au, the energy-versus-volume curves are calculated using 182, 168, and 168 (for the fcc, bcc, and hcp structures, respectively) $\mathbf{k}$ points in an irreducible wedge of the first Brillouin zone (IBZ). The charge density for Au is expanded with approximately 2300 plane waves corresponding to a cutoff energy of approximately 110 Ry. For the case of silver, we have used 280, 252, and 285 $\mathbf{k}$ points for the fcc, hcp, and bcc structures, respectively, and approximately 8000 plane waves for the charge-density expansion corresponding to a cutoff energy of 256 Ry.

Iteration to self-consistency is carried out until the total energy is stable to 10^{-5} Ry or better, corresponding to a maximum difference of 10^{-4} Ry or less between the Fourier components of the input and output screening potentials.

IV. RESULTS AND DISCUSSION

We have found that fairly large k point sets (over 150 k points in the IBZ) are required for the correct descriptions of the structural properties of Au and Ag, as it is evident from the k -point convergence test for the total energy, shown in Fig. 2 (for Au and for Ag with the numerical basis, respectively). From these figures, it can be seen that the hcp structure can be erroneously predicted to be the ground-state structure if an insufficient number of k points are used.

Total energies of bulk Au are calculated for different structures (fcc, bcc, and hcp with the ideal c/a ratio of 1.633). For each structure we have varied the lattice volume and the results are fitted to the universal binding curve,¹³

$$E(a) = \Delta E E^*(a^*), \quad (5)$$

with $a^* = (a - a_m)/l$ and $E^*(a^*) = (1 + a^*)\exp(-a^*)$, where ΔE , a_m , and l are scaling parameters. The value of ΔE is the cohesive energy per atom (the energy with respect to the free atom). The free-atom energy is obtained by taking the ground-state total energy of the pseudoatom, and adding a spin-polarization correction

FIG. 2. (a) The k -point-convergence test for the total energy of Au at the atomic volume of 118.37 a.u.³. The hcp structure is calculated at $c/a = 1.633$. (b) The k -point-convergence test for the total energy of Ag (with numerical local orbitals) at the atomic volume of 116.69 a.u.³. The hcp structure is taken at $c/a = 1.633$.

FIG. 3. The cohesive energy of Au as a function of atomic volume for different structures. The hcp structure is calculated at $c/a = 1.633$.

obtained from the total-energy difference between spin-polarized and unpolarized all-electron atomic calculation.¹⁴ The value of the energy for the Au isolated atom is -66.540 Ry. The coordinate a^* is a scaled length, a_m is the equilibrium lattice constant, and l is a scaling length related to the bulk modulus. The results are plotted in Fig. 3 and summarized together with the experimental values in Table IV. We found the fcc structure to be the most stable (the fcc energy is lower than the hcp energy by ~ 0.5 mRy/atom). There is good agreement between our calculations and the experimental values for the bulk properties. Since the energy between the fcc and the hcp structures is small, we have also optimized the c/a ratio for the hcp structure, keeping the atomic volume fixed at 118.37 a.u.³ (which is the equilibrium volume if the c/a ratio is at the "ideal" value). We found that a c/a ratio of 1.67 [larger than the ideal ratio $c/a = (\frac{8}{3})^{1/2}$] gives the lowest energy (see Fig. 4). Relaxation of the c/a ratio lowers the energy of the hcp phase by ~ 0.05 mRy. As a result, the energy of the hcp structure is still higher than the fcc structure by about ~ 0.4 mRy per atom. (We believe our calculations for the energy differences between different crystal structures are accurate to ~ 0.2 mRy, although it is difficult to make an accurate estimate of error bars in our calculations.)

In the case of silver, total energies are computed for the fcc, bcc, and hcp (with the ideal c/a ratio) structures. For each structure we have varied the lattice volume and

TABLE IV. Comparison of calculated and experimental values for bulk Au.

Struct.	Lattice constant (Å)	Lattice volume (Å ³)	Cohesive energy (eV/atom)	Bulk modulus (Mbar)
bcc		17.307	3.42	1.682
hcp ^a		17.277	3.45	1.871
fcc	4.104	17.282	3.46	1.790
Expt.	4.079	16.967	3.81	1.732

^a c/a ratio = 1.633.

TABLE V. Comparison of calculated and experimental values for bulk Ag.

Method and struct.	Lattice const. (Å)	Lattice vol. (Å ³)	Cohesive energy (eV/atom)	Bulk modulus (Mbar)
Gaussian:				
fcc	4.108	17.331	2.64	1.08
Numerical:				
fcc	4.115	17.417	3.01	0.961
hcp ^a		17.495	3.01	1.032
bcc		17.497	2.94	0.965
Experimental	4.090	17.105	2.95	1.007

^a c/a ratio = 1.633.

the results were fitted to the universal binding curve (free-atom energy for Ag is -74.904 Ry). The results are summarized, together with the experimental values in Table V, and shown in Fig. 5. The agreement between our calculations and the experimental values¹⁵ is again very good. At the ideal c/a ratio the hcp structure is less favorable than the fcc structure by ~ 0.04 mRy. When the c/a ratio is optimized (Fig. 6), we find that its optimum value is 1.67 (almost the same as in Au), lowering the energy of the hcp phase by ~ 0.1 mRy. As a result, the energy of the hcp structure is lower than the fcc structure by about ~ 0.06 mRy. The difference between the cohesive energies of the two structures in this calculation is less than 10^{-4} Ry, a value smaller than the precision of our method. A Gaussian-smearing scheme¹⁶ is used to determine the weight of the bands near the Fermi level when calculating the charge density and the band energy. We have used Gaussian widths of 0.2 eV for Au and 0.05 eV for Ag. Varying the Gaussian width down to 0.01 eV produces negligible changes in the results.

Out of curiosity about the effects of relativity on the bulk properties of solids, we have repeated our Au calculations with the nonrelativistic pseudopotential. The results, shown in Table VI, are quite interesting. The cohesive energy of nonrelativistic calculations is reduced by more than 1 eV, the lattice parameter is expanded by over 5%, and the bulk modulus is reduced by 42% over the corresponding results from the relativistic calculations. All these changes indicate that relativistic effects produce an increase in the bonding of the crystal. In fact, the bulk properties of the nonrelativistic calculation

TABLE VI. Comparison of calculated nonrelativistic Au with experimental values of bulk Au and Ag.

	Lattice constant (Å)	Lattice volume (Å ³)	Cohesive energy (eV/atom)	Bulk modulus (Mbar)
Au nonrel.	4.314	20.072	2.27	0.996
Expt.				
Au	4.079	16.967	3.81	1.732
Ag	4.090	17.105	2.95	1.007

FIG. 4. The total energy of hcp Au calculated for different c/a ratios at the atomic volume of 118.37 a.u.³

FIG. 5. The cohesive energy of Ag (with numerical local orbitals) as function of atomic volume for different structures. The hcp structure is calculated at $c/a = 1.633$.

FIG. 6. The total energy of hcp Ag for different c/a ratios at the atomic volume of 116.69 a.u.³

FIG. 7. The function f' for different values of α , and the radial function f (unnormalized).

bear such a resemblance to the properties of Ag (aside from the expanded lattice constant, which we can attribute to a larger core size in Au) that we conclude that the major factor for the difference in bulk properties of Au and Ag is that relativistic effects are much more important in Au than in Ag.

V. CONCLUSIONS

We have applied first-principles total-energy calculations to study the equilibrium ground-state properties of the noble metals Ag and Au. Norm-conserving pseudopotentials were used. The results for the equilibrium lattice constants, cohesive energies, and bulk modulus agree with the experimental values to within 1%, 9%, and 4%, respectively, for both Ag and Au. We have also shown that the relativistic effects are very important in explaining the differences in bulk properties of Au and Ag.

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FIG. 8. The test of the convergence of the total energy with respect to the plane-wave "cutoff" energy E_{cut} and with respect to α .

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APPENDIX A

Equation (4) gives the form of the numerical basis used for the local orbitals. We have chosen $r_c = 2.7$ a.u. (r_c is the radius for which f' is zero). Figure 7 shows f' (not normalized) for different values of α and the radial function $f(r)$. We have tested the convergence of the total energy with respect to the plane-wave cutoff energy E_{cut} and the coefficient α . The results are summarized in Fig. 8. We can see that for a big E_{cut} (18 Ry) the total energy is quite independent of α (because a large enough E_{cut} guarantees that the plane-wave part of the basis can make up for the inadequacy of the local orbitals). Also we can see that if E_{cut} is larger than 10.5 Ry, the optimal value of α is 0.7, and for this value, the total energy is virtually independent of E_{cut} . That is the reason we have chosen the values of 10.5 Ry and 0.7 for E_{cut} and α , respectively.

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