Ground state potential energy surfaces and bound states of M–He dimers (M=Cu,Ag,Au): A theoretical investigation

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We present an *ab initio* investigation on the ground state interaction potentials [potential energy surface (PES)] between helium and the group 11 metal atoms: copper, silver, and gold. To the best of our knowledge, there are no previous theoretical PESs proposed for Cu–He and Au–He, and a single one for Ag–He [Z. J. Jakubek and M. Takami, Chem. Phys. Lett. **265**, 653 (1997)], computed about 10 years ago at MP2 level and significantly improved by our study. To reach a high degree of accuracy in the determination of the three M–He potentials (M=Cu,Ag,Au), we performed extensive series of test computations to establish the appropriate basis set, the theoretical method, and the computational scheme for these systems. For each M–He dimer we computed the PES at the CCSD(T) level of theory, starting from the reference unrestricted Hartree–Fock wave function. We described the inner shells with relativistic small core pseudopotentials, and we adopted high quality basis sets for the valence electrons. We also performed CCSDT computations in a limited set of M–He internuclear distances, adopting a medium-sized basis set, such as to define for each dimer a CCSD(T) to CCSDT *correction term* and to improve further the quality of the CCSD(T) interaction potentials. The Cu–He complex has minimum interaction energy (E_{min}) of −28.4 μhartree at the internuclear distance of 4.59 Å (R_{min}), and the short-range repulsive wall starts at 4.04 Å ($R_{E=0}$). Quite interestingly, the PES of Ag–He is more attractive (E_{min} =−33.8 μhartree) but presents nearly the same R_{min} and $R_{E=0}$ values, 4.60 and 4.04 Å, respectively. The interaction potential for Au–He is markedly deeper and shifted at shorter distances as compared to the lighter complexes, with E_{min}=−69.6 μhartree, R_{min}=4.09 Å and $R_{E=0}$=3.60 Å. As a first insight in the structure of M–He$_n$ aggregates, we determined the rovibrational structure of the three M–He dimers. The Cu–He and Ag–He potentials support just few rotational excitations, while the Au–He PES admits also a bound vibrational excitation. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3020706]

I. INTRODUCTION

Helium is the only element that can be prepared in the fourth state of matter, the superfluid state. Helium nanodroplets, containing 10^3–10^4 atoms, represent an extremely cold and gentle environment for guest impurities (M). In fact, the ground state interactions between helium and any neutral chemical species are very weak, and hence the solvation process affects only slightly the electronic structure of the guest atom or molecular system.[1]

Apart from the intrinsic interest in the comprehension of the dynamical processes occurring in M–He$_n$ aggregates, the very peculiar properties of these systems represent an invaluable resource to conduct ultracold experiments with a high degree of accuracy, especially in the field of spectroscopy. The state of the art techniques permit the detection of very

subtle effects such as, for example, the small changes in the rovibrational structure of the host impurity induced by the surrounding superfluid medium. This has formed the basis for the spectacular He spectroscopic studies of Callegari *et al.*[2] and Choi *et al.*[3] Concerning the theoretical modeling of such phenomena, Szalewicz[4] recently pointed out that the determination of very precise M–He interaction potentials [potential energy surface (PES)] is a fundamental prerequisite for the simulations to be reliable, and to compare favorably with experiments. The case of the rovibrational spectrum of the OCS molecule in selected small helium aggregates is exemplary and proves how helpful the interplay between theory and experiments can be in pointing out the limits in both fields, in stimulating improvements, and in reaching a comprehensive understanding of the underlying dynamical processes.[5–8]

The picture becomes even more complex in the studies on the electronic structure of M–He$_n$ aggregates. In fact, during the electronic excitation and relaxation processes the system experiences very sudden changes in the interaction potential because the radial and the angular distributions of

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the repulsive walls and of the attractive wells of the PES might change dramatically from one electronic state to another. The main consequence is that quite often the electronic emission and absorption spectra of an isolated moiety change significantly after solvation by helium. The interpretation of the experimental data is subject to the knowledge of several excited state potentials and of quite complex phenomena, such as the formation of exciplets. Concerning the theoretical simulations, the vertical electronic transitions can be simulated reliably only when the structure of the $M-\text{He}_n$ aggregate in its initial state (i.e., the distribution in phase space of the nuclear wave function) has been characterized accurately, which reinforces the need for accurate ground state potentials. The studies conducted on quite simple systems, such as a single silver[9–14] or magnesium[15–17] atom dispersed in superfluid helium, are well representative of such difficulties.

In this article we present a detailed *ab initio* investigation on the ground state interaction potentials between helium and the group 11 metal atoms: copper, silver, and gold. This study is intended as the first step toward the theoretical modeling of the dynamics of small metal clusters in helium nanodroplets, which present many aspects of great interest. In fact, the unambiguous interpretation of spectroscopic data would be of great help in understanding the mechanisms underlying the formation of small metal clusters, the appearance of the metallic properties as their size increases, and the interplay between the metal atoms and the superfluid medium. Although these phenomena attracted growing experimental efforts in recent years, there are no studies devoted to Cu and Au atoms or clusters in superfluid helium, while the Ag_x-He_n aggregates are among the most studied systems.[10,12,18–27] The investigations conducted on silver aggregates in superfluid helium in the past decade cover a wide variety of structures, ranging from a single Ag atom,[10,12,20,27] to very small Ag_x clusters ($x<10$),[19,21–23] up to very complex aggregates containing thousands of atoms.[18,24–26]

As concerns the theoretical investigations on $M_x-\text{He}_n$ ($M=\text{Cu},\text{Ag},\text{Au}$), to the best of our knowledge, there are just four studies on $\text{Ag}-\text{He}_n$ available in literature, and none on Cu–He and Au–He. The studies on $\text{Ag}-\text{He}_n$ date back to 1996 (Ref. 10) and 1997 (Ref. 11) and report *ab initio* computations on the interaction potential for the Ag–He dimer in the ground and in various excited states. These PESs have then been used to simulate electronic transition processes in $\text{Ag}-\text{He}_n$ systems.[11,13,14] Based on the results presented here, we believe that the accuracy of the ground state PES originally proposed for Ag–He is now largely improved, and the same should be done for the excited states before performing further theoretical simulations of complex dynamical processes. As for Cu–He and Au–He dimers, we present here the first systematic *ab initio* study on these systems and determine for the first time an analytical expression for their ground state interaction potentials.

This article is organized as follows. Sections II A and II B contain a survey of the *ab initio* test computations that we carried out to define an appropriate computational scheme for $M-\text{He}$ complexes ($M=\text{Cu},\text{Ag},\text{Au}$). Section II C reports on the determination of a set of high quality interaction energies for these systems and on the definition of the

analytical two-body PES for their electronic ground states. The main features of the interaction potentials are presented in Sec. III A and compared to literature results, and the rovibrational structures of $M-\text{He}$ dimers ($M=\text{Cu},\text{Ag},\text{Au}$) are discussed in Sec. III B. Conclusions and perspectives are presented in Sec. IV.

II. COMPUTATIONAL DETAILS

To reach a high degree of accuracy in the determination of the potential energy surfaces for the $M-\text{He}$ complexes ($M=\text{Cu},\text{Ag},\text{Au}$) in their electronic ground states, we conducted two extensive series of test computations, focused on the definition of the appropriate theoretical method and the basis set. In the first tests we selected one medium-sized basis set, and for every $M-\text{He}$ dimer we evaluated the performance of various theoretical methods and computational approaches. In all computations the metal atoms have been described with the relativistic small core pseudopotentials (PPs) proposed by Figgen *et al.*[28] These PP include the 10 inner electrons for copper, 28 for silver, and 60 for gold. Every metal atom is therefore left the 19 outer electrons, corresponding to the following scheme for the electronic structure: ([Ne]-PP) $3s^23p^63d^{10}4s^1$ for copper, ([Ar]$3d^{10}$-PP) $4s^24p^64d^{10}5s^1$ for silver, and ([Kr]$4d^{10}4f^{14}$-PP) $5s^25p^65d^{10}6s^1$ for gold. We included in correlated calculations the two $1s^2$ electrons of helium, plus one among three different sets of active electrons for the metal atoms: W1, 19 active electrons on the metal $(n-1)s^2(n-1)p^6(n-1)d^{10}ns^1$ (with $n=4$, 5, and 6 for Cu, Ag, and Au, respectively); W2, 17 active electrons $(n-1)p^6(n-1)d^{10}ns^1$; and W5, 11 active electrons $(n-1)d^{10}ns^1$. The reference wave function for all computations comes from PP unrestricted Hartree–Fock (UHF) calculations. The correlation contributions have been determined using the Møller–Plesset (MP) and the coupled-cluster (CC) methods at various degrees of accuracy. The MP2 and MP4 results have been obtained with the GAMESS code.[29] The interaction energies at the various CC levels [singles and doubles, CCSD;[30,31] singles and doubles with a perturbative triples correction, CCSD(T);[32] singles, doubles and triples, CCSDT[33,34]] have been determined using GAUSSIAN-03 (Ref. 35) and ACES-II.[36]

In the second series of tests we selected just one computational approach (MP4, W2 set of active electrons), and we evaluated the performance of several combinations of basis sets having different nature and size. First we focused on Ag–He, and we determined the role of diffuse Gaussian functions centered on the helium and the silver atom and of the *bond functions* placed along the Ag–He internuclear axis. Then we tested the complete aug-cc-pVnZ-PP ($n=2-5$) series for Cu, Ag, and Au atoms,[37] and both the aug-cc-pVnZ and the d-aug-cc-pVnZ ($n=2-5$) series for He,[38] plus a set of bond functions placed at midway along the $M-\text{He}$ internuclear axis. As will emerge from the discussion below, the data analysis of the overall tests series gives clear indications on the proper combination of the theoretical method and basis sets required to compute very accurate potentials.

TABLE I. Properties of the ground state interaction potentials of M−He (M=Cu,Ag,Au) computed with different theoretical methods. In all the computations we adopted the aug-cc-pVDZ basis set for all atoms, plus the $3s3p2d$ set of bond functions; the counterpoise scheme has been used to correct the interaction energy data for BSSE; energies in μhartree; distances in Å.

Method	Active electrons[a]	E_{min}[b]	R_{min}[c]	$R_{E=0}$[d]	$E_{R=3.00}$[e]
		Ag–He			
MP2	W5	−32.9	4.60	4.06	1502
MP2	W2	−44.9	4.48	3.91	1428
MP2	W1	−45.8	4.49	3.92	1440
MP4	W5	−32.3	4.68	4.09	1482
MP4	W2	−44.2	4.52	3.94	1403
MP4	W1	−46.0	4.52	3.94	1413
CCSD(T)	W5	−23.0	4.87	4.23	1496
CCSD(T)	W2	−26.3	4.78	4.12	1442
CCSD(T)	W1	−27.5	4.75	4.12	1452
CCSDT	W5	−23.2	4.92	4.22	1489
CCSDT	W1	−28.5	4.73	4.14	1441
		Cu–He			
MP2	W1	−34.0	4.53	3.97	1203
MP4	W5	−47.5	4.41	3.84	1086
MP4	W2	−74.1	4.18	3.65	973
MP4	W1	−84.1	4.12	3.63	988
CCSD(T)	W5	−19.9	4.85	4.28	1231
CCSD(T)	W2	−21.7	4.82	4.21	1200
CCSD(T)	W1	−23.0	4.77	4.17	1218
CCSDT	W1	−25.1	4.72	4.13	1199
		Au–He			
MP2	W1	−83.1	4.06	3.57	926
MP4	W5	−60.6	4.15	3.67	1006
MP4	W2	−74.5	4.01	3.60	945
MP4	W1	−75.1	4.03	3.61	950
CCSD(T)	W5	−49.6	4.24	3.72	1041
CCSD(T)	W2	−55.4	4.19	3.70	1004
CCSD(T)	W1	−56.1	4.20	3.70	1009
CCSDT	W1	−57.9	4.19	3.73	998

[a]Electrons included in correlation calculations, see text for details.
[b]Minimum interaction energy estimated by square polynomial interpolation of the three points with lower—i.e. large and negative—interaction energy.
[c]Internuclear distance at the minimum interaction energy.
[d]Internuclear distance where the interaction energy equals zero, estimated by square polynomial interpolation of the three points with smaller—i.e. closer to zero in absolute value—interaction energy.
[e]Interaction energy at the internuclear distance of 3.00 Å.

A. Methods

We collected in Table I some properties of the interaction potentials for Cu–He, Ag–He, and Au–He computed with several theoretical methods and computational schemes, and a graphical landscape of these results is reported in Fig. 1. In all cases we adopted the aug-cc-pVDZ basis set for the metal atom and for helium, plus the $3s3p2d$ set of bond functions originally proposed by Tao *et al.*,[39] located at midway along the M−He internuclear axis. We always adopted the counterpoise scheme to correct the interaction energies for basis set superposition error (BSSE).

Let us start with the analysis of the correlation contribution to the interaction energy (E_{int}) coming from the electrons belonging to the metal atoms. As can be seen in Fig. 1, in all M−He systems the UHF interaction energy curve is entirely repulsive, and hence the attractive well of the poten-

tial is entirely due to correlation effects. At long range (i.e., in the attractive region of the PES), all the electrons of the metal atoms included in Møller–Plesset and CC computations give an attractive contribution to the interaction, and hence the PES become more and more attractive as we compare W1 to W2 and to W5 curves. Accordingly, the potential well shifts toward shorter distances. For any given M−He complex and theoretical method [MP4, CCSD(T), and CCSDT], W1 and W2 results are very close to each other, while W5 ones are markedly different. Quantitatively, the estimate of the well depth (E_{min}) changes by about 1 μhartree as we compare W1 and W2 data, while from W2 to W5 we observe much larger variations, reaching 2−5 μhartree at the CCSD(T) level of theory and 10−20 μhartree for MP4 results. The only exception is observed for MP4 calculations on the Cu–He dimer, where the
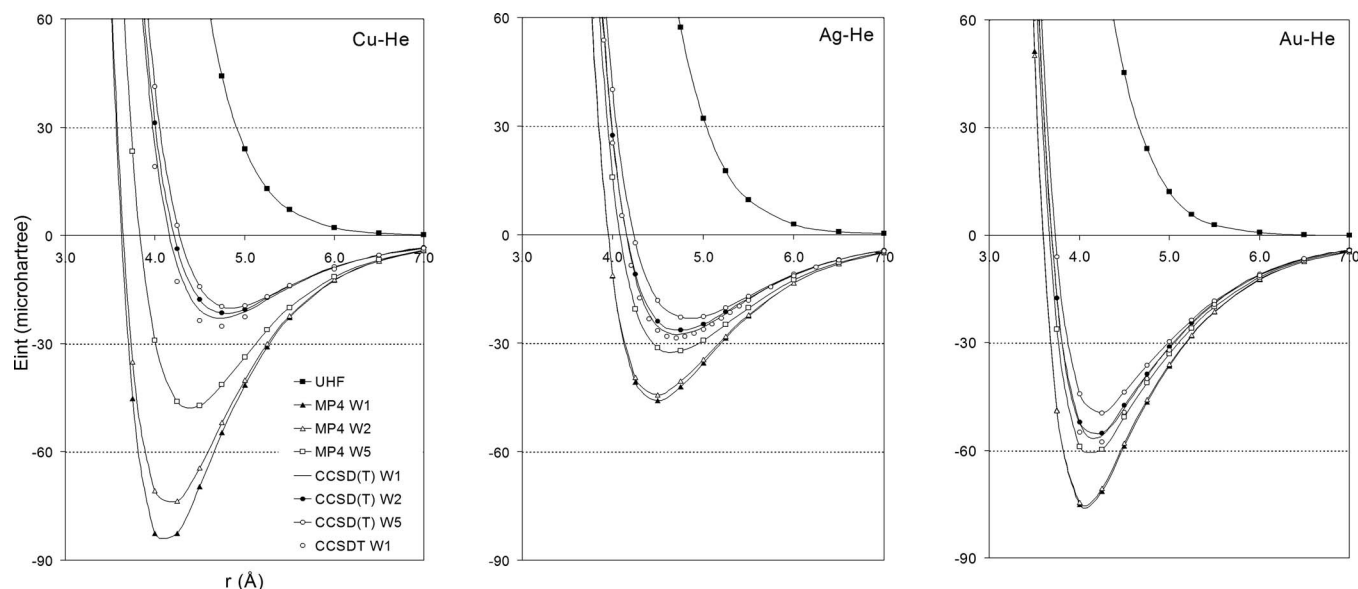
FIG. 1. Interaction energy of M–He complexes (M=Cu,Ag,Au) determined with different theoretical approaches (see text for details). In all computations we adopted the aug-cc-pVDZ basis set for all atoms, plus the $3s3p2d$ set of bond functions. The full lines are guides to the eyes.

W1 to W2 difference in E_{min} is about ten times larger than in the other cases. However, also in this system the W2 to W5 variation is much larger than the W1 to W2 one (27 and 13 μhartree, respectively). Concerning the distribution of the interaction potentials along the M–He internuclear distance, the estimates of R_{min} and $R_{E=0}$ determined at W1 and W2 levels are nearly identical, while the W5 predictions are larger by about 0.10 Å. These variations are consistent with the differences registered for the interaction energies. In conclusion, the attractive part of the interaction potential of all dimers is properly described when the correlation includes the W2 set of electrons, i.e., the outermost s, p, and d shells of the metal atom, along with the $1s^2$ electrons of He.

In this test series we also sampled the repulsive wall of the potentials at the M–He internuclear distance of 3.00 Å. Whatever the theoretical approach the W1 and W2 results are very close to each other (see Table I), with differences limited to 10–20 μhartree to be compared with interaction energies of about 10^3 μhartree. The W1 to W5 difference presents a wide range of values depending on the M–He complex and on the theoretical method adopted. However, the values are always much larger than the corresponding W1 to W2 ones, and in some cases reach nearly 10^2 μhartree, which represents about 10% of the interaction energy. Interestingly, in the repulsive wall the correlation contributions of the electrons of the metal atom are not always attractive. In fact, in all systems and methods considered, at 3.00 Å the W2 interaction energy is lower (i.e., less repulsive) than the W1 one, and hence the overall correlation contribution to the interaction energy of the $(n-1)s^2$ shell (with $n=4$, 5, and 6 for Cu, Ag, and Au, respectively) changes in sign, from attractive to repulsive, as the He atom approaches the metal.

As concerns the performance of the theoretical methods tested (Møller–Plesset and CC), the data in Table I contradict the feature registered in many theoretical studies on weakly bound complexes, where the MP4 PES is very close to and less attractive than the CCSD(T) one.[40,41] In the Cu–He, Ag–He, and Au–He dimers, the well depth of the MP4 potential is much larger than the CCSD(T) one, and the energy differences have the same order of magnitude of the minimum interaction energy. Consistently, the MP4 potentials are shifted at shorter distances as compared to CCSD(T) ones, in the measure of 0.2–0.6 Å depending on the system considered. It is straightforward to predict that the choice among the MP4 and the CCSD(T) potentials would be determinant in the theoretical simulation of Cu–He$_n$, Ag–He$_n$ and Au–He$_n$ aggregates because the structural properties of these systems are usually very sensitive even to subtle changes in the interaction potentials.[4] We registered an analogous performance of the Møller–Plesset scheme in our previous investigation on the Mg–He complex,[17] but this system presents much smaller differences between the MP4 and the CCSD(T) approaches. In fact, the well depth of the MP4 potential for Mg–He—computed with a high quality basis set—is larger by about 5 μhartree than the CCSD(T) one, which is about 20% of the minimum interaction energy. Conversely, in the M–He (M=Cu,Ag,Au) complexes this values range from about 20 (Au, Ag) to 50 μhartree (Cu), and represent 25% (Au), 40% (Ag), and 60% (Cu) of the corresponding minimum interaction energies. An important feature common to M–He complexes (M=Mg,Cu,Ag,Au) is that CCSDT results are slightly more attractive and very close to CCSD(T) ones (see Table I for noble metal atoms, and previous theoretical studies for Mg–He).[17,42]

The MP4 to CCSD(T) energy differences in the repulsive region of the potential (i.e., at 3.00 Å) are consistent with the above description. The MP4 interaction potentials are markedly less repulsive than the CCSD(T) ones, and the differences range from about 50 (Ag, Au) to 200 μhartree (Cu), to be compared with interaction energies of 1000–1500 μhartree, and an overall correlation contribution to the interaction energy of about 500 μhartree. As happens in the attractive region of the PES, the CCSD(T) data are

very close to the CCSDT ones, and the interaction energy differences never exceed 1% of the interaction energy.

The different performances of the Møller–Plesset and the CC approaches should not be attributed to the different treatments of the spin contamination, a possible fallout when using UHF reference wave functions. In fact, we carried out a limited set of computations for the three complexes at the MP4 and the CCSD(T) levels of theory, adopting the Restricted open shell Hartree–Fock (ROHF) solution instead of the UHF one. In all M–He systems, and for all the internuclear distances considered, to remove the spin contamination increases instead of decreasing the difference between the MP4 and the CCSD(T) interaction potentials. More precisely, the CC interaction energies remain nearly unchanged, with variations limited to 0.1 μhartree in the attractive part of the PES and lower than 0.5 μhartree even in the repulsive wall, where E_{int} is larger than 10^3 μhartree. Conversely, when the ROHF reference is adopted the MP4 potential becomes sensibly more attractive. In the attractive region of the PES the differences in E_{int} range from about 1 to 4 μhartree depending on the distance and the metal atom considered, and in the repulsive wall these values range from 5 to 10 μhartree.

The CC theory represents the most accurate tool among the practical *ab initio* methods[43] and was proved to provide correct results even when computing the interaction energies of very weakly bound complexes.[42] In a study on two systems quite similar to the ones investigated by us, the Ca–He and the Mg–He dimers, Hinde[42] showed that when CC computations include single, double, and triple excitations, the results have nearly the same quality of full configuration interaction ones, which are by far more expensive computationally. On the basis of the above discussion we conclude that the Møller–Plesset expansion performs quite poorly in weakly bound complexes between helium and neutral metal atoms, as compared to the CC method. In these systems the CCSD(T) level is adequate for computing very accurate PES, and it recovers about 98% of the correlation energy contributions to the interaction energy as compared to the CCSDT approach.

B. Basis sets

To select the appropriate basis set combination, we carried out a series of total energy Møller–Plesset computations at the MP4 level of theory. The choice of the method is based on the assumption that it recovers properly the trend of the correlation contributions to the interaction potential as the size of the basis set increases even if the interaction energies predicted are not very accurate. We selected a very limited set of M–He internuclear distances, and we correlated just the W2 set of electrons. We collected in Table II the estimates of the minimum interaction energy, the corresponding internuclear distance, and the distance where the PES becomes repulsive for all systems and basis sets considered. These results come simply by square polynomial interpolations of sets of three interaction energies (see the caption of Table II for details), and hence they are quite rough estimates of the corresponding PES. However, let us remark that the

scope of the tests discussed in this section is not to compute reliable interaction energies but just to determine the performance of various basis sets combinations in recovering the correlation contributions to the interaction energy in M–He complexes.

Analogous to Sec. II A, we carried out a complete series of tests on Ag–He, and repeated only the most significant ones on Cu–He and Au–He. The analysis of the data collected in Table II for the Ag–He complex provides very simple rules concerning the basis set convergence.

(1)   The bond functions are very efficient in recovering interaction energy. Adopting the medium-sized aug-cc-pVTZ set for both metal and helium atoms, and no bond functions (for a total of 111 Gaussian functions), we obtained a well depth of −42 μhartree, quite far from the value of about −54 μhartree obtained with the largest basis set adopted, from now on referred to as *best* (aug-cc-pV5Z for Ag, d-aug-cc-pV5Z for He, $3s3p2d$ bond functions, for a total of 324 Gaussian functions). Significant deviations are observed also for R_{min} and $R_{E=0}$, respectively, 0.1 and 0.3 Å larger than the best values. The much smaller aug-cc-pVDZ set, adopted for both M and He atoms, with the inclusion of the $3s3p2d$ set of bond functions (85 Gaussian basis functions), provides estimates of E_{min}, R_{min}, and $R_{E=0}$ much closer to the best values. Let us note also that the aug-cc-pVTZ basis set, adopted for both atoms, plus the $3s3p2d$ set of bond functions (133 total basis functions), provides an interaction potential very close to the one obtained with the best basis set. In fact, the error in the estimate of the energy minimum reduces to 2 μhartree, R_{min} is larger by just 0.03 Å, and a somewhat larger error is found for $R_{E=0}$, 3.76 Å to be compared with the best value of 3.68 Å.

(2)   The diffuse functions are fundamental in the determination of the PES, and a set must be placed both on the metal and on the helium atoms. In fact, let us consider the various (d-)(aug-)cc-pVTZ combinations selected for the Ag–He complex. Adopting the cc-pVTZ set for both Ag and He (99 Gaussian, including the bond functions) gives a much worse description of the PES (E_{min}=−31.7 μhartree) as compared—for example—to the smaller aug-cc-pVDZ basis set (85 basis functions, E_{min}=−45.8 μhartree). To place a set of diffuse functions on just one atom produces significant improvements in the estimates of E_{min}, R_{min}, and $R_{E=0}$, and the performance improves further and significantly from a quantitative point of view, when the diffuse functions are adopted on both atoms. Conversely, to supplement the aug-cc-pVnZ basis set for helium atom with a second set of diffuse functions (d-aug-cc-pVnZ sets) gives very small contribution to the interaction potential, and the changes in the estimates of E_{min} and $R_{E=0}$ are limited to about 0.5 μhartree and 0.01 Å, while no noticeable changes are observed on R_{min}.

(3)   The interaction potential is nearly converged when computed with the aug-cc-pVQZ basis set for Ag and the d-aug-cc-pVQZ on He, plus the $3s3p2d$ set of bond

TABLE II. Properties of the ground state interaction potentials of M–He (M=Cu, Ag, Au) computed with different basis sets. The data reported here correspond to MP4 computations with the W2 set of active electrons; the $3s3p2d$ set of bond functions has been added to the atomic basis sets in all cases but one, reported in italic; we adopted the counterpoise scheme to correct the interaction energy data for BSSE; the properties of the PES have been estimated using just three points for each dimer: 3.50, 4.00 and 4.50 Å for Cu–He and Au–He, and 4.00, 4.50, and 5.00 for Ag–He, and hence equivalent entries presented both in Tables I and II might differ from each other; energies in μhartree; distances in Å.

M basis set	He basis set	Basis functions[a]	E_{min}[b]	R_{min}[c]	$R_{E=0}$[d]
		Ag–He			
cc-pVTZ	cc-pVTZ	99	−30.7	4.71	4.15
aug-cc-pVTZ	cc-pVTZ	124	−39.7	4.64	3.95
cc-pVTZ	aug-cc-pVTZ	108	−43.9	4.66	3.96
aug-cc-pVDZ	aug-cc-pVDZ	85	−45.8	4.64	3.90
aug-cc-pVDZ	d-aug-cc-pVDZ	89	−45.2	4.64	3.91
aug-cc-pVTZ	*aug-cc-pVTZ*	*111*	*−41.9*	*4.67*	*3.99*
aug-cc-pVTZ	aug-cc-pVTZ	133	−52.2	4.57	3.76
aug-cc-pVTZ	d-aug-cc-pVTZ	142	−52.7	4.57	3.76
aug-cc-pVQZ	aug-cc-pVQZ	203	−53.7	4.54	3.70
aug-cc-pVQZ	d-aug-cc-pVQZ	219	−54.1	4.54	3.69
aug-cc-pV5Z	aug-cc-pV5Z	299	−53.9	4.54	3.68
aug-cc-pV5Z	*d-aug-cc-pV5Z*	324	−54.2	4.54	3.68
		Cu–He			
aug-cc-pVDZ	aug-cc-pVDZ	85	−87.2	4.23	3.70
aug-cc-pVDZ	d-aug-cc-pVDZ	89	−86.6	4.23	3.70
aug-cc-pVTZ	aug-cc-pVTZ	133	−104.1	4.18	3.59
aug-cc-pVTZ	d-aug-cc-pVTZ	142	−104.8	4.18	3.59
aug-cc-pVQZ	aug-cc-pVQZ	203	−108.1	4.17	3.55
aug-cc-pVQZ	d-aug-cc-pVQZ	219	−108.6	4.17	3.55
aug-cc-pV5Z	aug-cc-pV5Z	299	−109.1	4.16	3.54
aug-cc-pV5Z	d-aug-cc-pV5Z	324	−109.5	4.16	3.54
		Au–He			
aug-cc-pVDZ	aug-cc-pVDZ	85	−85.7	4.19	3.64
aug-cc-pVDZ	d-aug-cc-pVDZ	89	−84.2	4.19	3.64
aug-cc-pVTZ	aug-cc-pVTZ	133	−93.2	4.17	3.56
aug-cc-pVTZ	d-aug-cc-pVTZ	142	−93.8	4.17	3.56
aug-cc-pVQZ	aug-cc-pVQZ	203	−95.3	4.15	3.52
aug-cc-pVQZ	d-aug-cc-pVQZ	219	−95.8	4.15	3.52
aug-cc-pV5Z	aug-cc-pV5Z	299	−95.5	4.15	3.51
aug-cc-pV5Z	d-aug-cc-pV5Z	324	−95.9	4.15	3.51

[a]Total number of basis functions ($5d$, $7f$).
[b]Minimum interaction energy.
[c]Internuclear distance at the minimum interaction energy.
[d]Internuclear distance where the interaction energy equals zero.

functions (219 Gaussian functions). Further improvements in the quality of the basis set, up to 324 basis functions, produce very limited changes in the properties of the PES: E_{min} lowers by just 0.1 μhartree, $R_{E=0}$ decreases by 0.01 Å, and R_{min} does not change at all. From now on, this set will be referred to as *converged*.

(4) The aug-cc-pVDZ set for both atoms plus the $3s3p2d$ bond functions (85 Gaussian basis functions) is the smallest combination that provides an acceptable description of the interaction potential. In fact, this Gaussian set recovers about 85% of the converged well depth, and the errors on R_{min} and $R_{E=0}$ are about 0.1 and 0.2 Å, respectively, 2.5% and 5% overestimated as compared to the best results.

We assumed that points (1) and (2) are valid also in the Cu–He and the Au–He dimers, and we focused just on points

(3) and (4). The Au–He complex behaves similar to the Ag–He one. First, the potential obtained with the aug-cc-pVQZ set for Au and the d-aug-cc-pVQZ set for He plus bond functions is nearly identical to the one obtained with the much larger aug-cc-pV5Z (Au)/d-aug-cc-pV5Z (He) one. Second, the adoption of the aug-cc-pVDZ set for both atoms, plus the $3s3p2d$ bond functions, provides a reasonable description of the interaction potential, and the estimate of E_{min} is just 10% smaller as compared to the best data, while R_{min} and $R_{E=0}$ are slightly overestimated (about 1% and 5%, respectively). The picture is slightly less favorable in the Cu–He complex because the convergence rate of the PES at increasing basis set size is somewhat less efficient. In fact, the aug-cc-pVQZ (Cu)/d-aug-cc-pVQZ (He)/$3s3p2d$ (bond functions) interaction potential is about 1% less attractive than the best one, while R_{min} and $R_{E=0}$ are already converged.
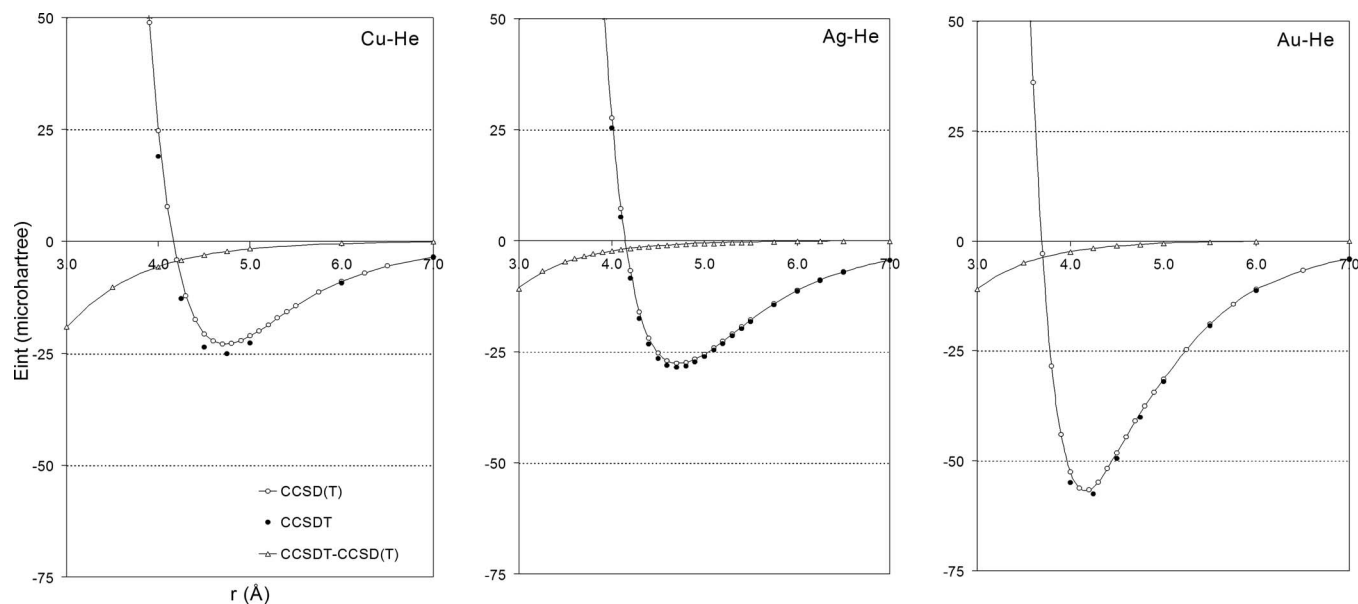
FIG. 2. Interaction potentials of M–He complexes (M=Cu,Ag,Au) computed at the CCSD(T) and the CCSDT levels of theory, along with the curve of the energy difference between the two methods. Interaction energies have been determined adopting the aug-cc-pVDZ basis set for all atoms, plus the $3s3p2d$ set of bond functions. The CCSD(T) lines are guides to the eyes. The CCSDT-CCSD(T) lines represent the fitting of the CCSDT minus CCSD(T) interaction energy difference, as described in Sec. II C.

Furthermore, when the aug-cc-pVDZ basis set plus bond functions is adopted, the well depth is underestimated by 20% as compared to the best values, with R_{min} and $R_{E=0}$ values overestimated by about 1%–5%.

In conclusion, the adoption of the aug-cc-pVQZ and the d-aug-cc-pVQZ basis sets for the metal and the He atoms, respectively, plus the $3s3p2d$ set of bond functions, ensures that the interaction energies of Cu–He, Ag–He, and Au–He dimers are nearly converged, with some minor discrepancy in the lighter complex. Second, the aug-cc-pVDZ basis set plus bond functions allows determining reasonable interaction energies (from 80% to 90% of the best values) with the smallest computational effort possible.

C. The determination of the PES

We defined a single computational procedure for the determination of the ground state interaction potential of the three intermolecular complexes under investigation. First, we included in correlation calculations the W1 sets of electrons in all systems because the W2 to W1 difference is small but not negligible, and the increase in computational requirements not too heavy. Second, we performed only CC calculations because the performance of the Møller–Plesset expansion is not satisfactory in these systems. Third, the complete interaction potentials have been computed at the CCSD(T) level of theory, adopting the aug-cc-pVQZ basis set for the metal atoms, the d-aug-cc-pVQZ one for He, and placing the $3s3p2d$ set of bond functions midway along the internuclear axis. Fourth, we determined the interaction energy of each complex at 30 internuclear distances, selected to sample accurately the regions of the PES relevant to the simulation of metal atoms in superfluid helium (i.e., at very cold temperatures): the attractive well and the portion of the repulsive wall where the interaction energy is lower than or comparable to the absolute value of E_{min}. We selected the following set of distances for Cu–He and Ag–He: 3.00, 3.25, and 3.50 Å (highly repulsive wall); from 3.50 to 5.50 with 0.10 Å steps (slightly repulsive wall and attractive well); 5.75, 6.00, 6.25, 6.50, 7.00, 8.00, and 10.00 Å (long-range attractive tail). In the case of Au–He we used a slightly different set because its PES is shifted toward shorter distances: 2.75 and 3.00 Å; from 3.10 to 5.00 with 0.10 Å steps, plus 5.25, 5.50, 5.75, 6.00, 6.50, 7.00, 8.00, and 10.00 Å.

We have shown in Sec. II B that the aug-cc-pVDZ basis set adopted for both the metal and the He atoms, plus the $3s3p2d$ set of bond functions, gives a reasonable description of the PES. In the Ag–He complex we determined the interaction energy with this basis set, at the CCSD(T) and the CCSDT levels of theory, in the complete set of 30 internuclear distances. As reported in Fig. 2, the difference between the two methods is small (i.e., negligible as compared to the total correlation energy) along the entire PES and increases very smoothly at decreasing internuclear distances. Moving from the aug-cc-pVDZ basis set for both the metal and the helium atoms to the converged set (aug-cc-pVQZ for the metal atom, d-aug-cc-pVQZ for helium, $3s3p2d$ bond functions), the changes in correlation energy are limited to 10% in the case of Ag–He, and hence we are confident that the CCSD(T) to CCSDT energy differences computed with the *small* basis set represent a reliable approximation of the converged CCSDT values. In the other M–He complexes we reduced to 9 (Cu–He) and to 10 (Au–He) the number of internuclear distances considered for CCSDT computations, and we adopted the small basis set described above. In fact, the CCSDT to CCSD(T) difference function is extremely smooth also in these complexes, as can be seen in Fig. 2, and hence there is no need to sample this curve with a fine grid.

Most techniques to simulate dynamical processes require a continuous representation of the system potential energy surface. The analytical CCSD(T) interaction potentials for
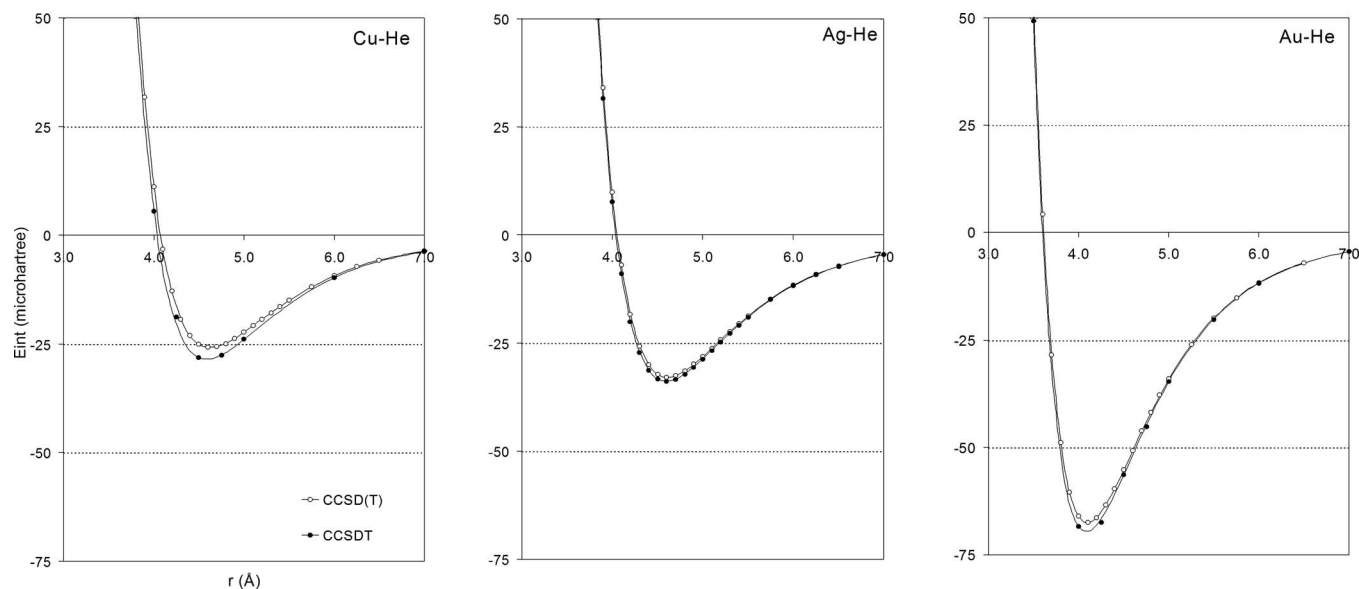
FIG. 3. Analytical CCSD(T) and CCSDT ground state interaction potentials for the M–He complexes (M=Cu, Ag, Au). Empty circles: CCSD(T) energy values computed with the converged basis set (see text for details). Full circles: sum between the CCSD(T) energy values computed with the converged basis set, and the CCSD(T) to CCSDT energy difference computed with the aug-cc-pVDZ basis set for all atoms, plus the $3s3p2d$ set of bond functions.

the M–He complexes (M=Cu, Ag, Au) have been obtained by interpolation of the interaction energy values obtained at the CCSD(T) level of theory with the converged basis set. The analytical expression includes quintic splines smoothly (i.e., with a continuous first derivatives) joined at 10.00 Å with a polynomial term of the form C_6/R_{M-He}^6 to describe the long-range tail of the PES. To improve the quality of these potentials, we fitted the CCSD(T) to CCSDT energy differences—obtained with the smaller basis set—using the simple analytical expression $A \exp[-b(R_{M-He}-R_0)]$, where A, b, and R_0 are free parameters separately optimized for each complex. As reported in Fig. 2, this functional form proved adequate in the entire range of internuclear distances spanned by the *ab initio* computations. The summation between the CCSD(T) potential and the analytical CCSD(T) to CCSDT correction function generates a second set of PES for the M–He dimers, in the following referred to as CCSDT potentials. Although these PES do not come directly from CCSDT computations adopting a converged basis set, based on the discussion of the preceding paragraphs we are confi-

dent that the CCSDT interaction potentials closely reproduce quantum mechanical CCSDT results.

III. RESULTS

A. Properties of the interaction potentials

A pictorial view of the analytical CCSD(T) and CCSDT potentials for the three M–He complexes is reported in Fig. 3, and their main features are collected in Table III. First of all, in all complexes the difference between the CCSSD(T) and the CCSDT PES is noticeable only in the proximity of the bottom of the attractive well. In fact, at distances larger than R_{min} the two curves are nearly indistinguishable, as shown in Fig. 3, while at shorter distances the CCSD(T) to CCSDT difference increases very smoothly, and hence it becomes negligible along the entire repulsive wall, as properly summarized by the values of $E_{R=3.00}$ reported in Table III.

Let us now compare the potentials of the three M–He systems (M=Cu, Ag, Au). When the atomic number of the metal atom increases, the attractive well becomes deeper and

TABLE III. Properties of the analytical ground state potentials of the M–He complexes (M=Cu, Ag, Au). Energies in μhartree; distances in Å.

System	Potential	E_{min} [a]	R_{min} [b]	$R_{E=0}$ [c]	$E_{R=3.00}$ [d]	λ [e]
Cu–He	CCSD(T)	−25.8	4.63	4.07	1101	2.7
Cu–He	CCSDT	−28.4	4.59	4.04	1082	2.9
Ag–He	CCSD(T)	−32.9	4.61	4.05	1324	3.4
Ag–He	CCSDT	−33.8	4.60	4.04	1314	3.5
Au–He	CCSD(T)	−67.5	4.10	3.61	887	6.2
Au–He	CCSDT	−69.6	4.09	3.60	876	6.4

[a]Minimum interaction energy.
[b]Internuclear distance at the minimum interaction energy.
[c]Internuclear distance where the interaction energy equals zero.
[d]Interaction energy at the M–He internuclear distance of 3.00 Å.
[e]Dimensionless parameter designed to foresee the onset of the solvation process of an impurity in liquid helium, see Ref. 44.

shifted to shorter M–He internuclear distances. The same shift is observed for the position of the repulsive wall. However, quantitatively the Cu–He and Ag–He PESs are quite similar to each other, while Au–He is markedly different. The well depth of Ag–He is about 30% larger than the Cu–He one, with E_{min}=−32.9 and −33.8 μhartree in Ag–He at the CCSD(T) and CCSDT levels, to be compared with the values of −25.8 and −28.4 μhartree obtained for Cu–He. In the Au–He potential, E_{min} is two times larger as compared to the lighter complexes, with E_{min}=−67.5 and −69.6 μhartree in the CCSD(T) and CCSDT PES. Furthermore, the Cu–He and the Ag–He potentials have the same values of R_{min} and $R_{E=0}$, about 4.60 and 4.05 Å, while the PES of the Au–He complex is shifted to shorter distances in the considerable amount of about 0.5 Å (R_{min}=4.1 Å, $R_{E=0}$=3.6 Å). Considering the similar values of R_{min} and of $R_{E=0}$ in Cu–He and Ag–He, we believe that it would be intriguing to study comparatively He$_n$ aggregates doped with these metal atoms, as a possible way of disentangling the effect of the other parameters—such as the well depth and its overall curvature—on the structural properties of metal-seeded helium nanodroplets.

Another important point is the validation of the very simple model proposed by Ancilotto *et al.*[44] to foresee the solvation of impurities in He$_n$ aggregates. These authors introduced a dimensionless parameter defined as λ =$2^{-1/6}\sigma^{-1}\rho\varepsilon r_e$, where σ is the surface tension of liquid He, ρ is the number density of bulk He, ε and r_e are the minimum interaction energy and the corresponding internuclear distance of the two-body M–He potential, respectively. An impurity M should be solvated by superfluid helium when λ is larger than 1.9, otherwise M resides at the surface of the liquid. According to this model, copper, silver, and gold atoms should be solvated by helium because the corresponding λ values are well beyond the threshold value (see Table III). However, in the case of Cu–He, λ falls within the same range determined in the case of Mg–He, from 2.7 to 3.1 depending on the potential adopted,[17,42] and we have shown that the solvation process of magnesium presents quite unusual and ubiquitous features.[17] The comparison between the properties of Cu–He$_n$ and Mg–He$_n$ is a further reason of interest in this system.

To the best of our knowledge, there are no theoretical investigations on Cu–He and Au–He available in literature, and hence there is no reference to compare the PES proposed by us. Concerning Ag–He, a single research group conducted two theoretical investigations on its ground and several excited states potentials, and these studies date back to about 10 years ago.[10,11] In the first paper Persson *et al.*[10] presented MP4 computations on the UHF reference and proposed a PES with E_{min}=−87 μhartree at the internuclear distance of 4.3 Å, nearly three times more attractive than our potential, and shifted at shorter distances by about 0.3 Å. In a second investigation, Jakubek and Takami[11] computed the potential at UHF-MP2 level, obtaining for the PES the values of E_{min}=−51.5 μhartree at R_{min}=4.42 Å. This potential is about 50% more attractive than the CC PES determined by us, and shifted at short distances by about 0.2 Å. These results are consistent with the general performance of the

Møller–Plesset expansion in comparison with the CC method when applied to complexes between neutral metal atoms and helium. The PES proposed by Jakubek and Takami[11] has been adopted in the quantum mechanical simulations of Ag–He$_n$ aggregates performed in recent years.[13,14] The large differences with respect to CC results suggest that repeating these simulations using the PES proposed by us might prove useful.

B. Rovibrational structure

The main properties of the rovibrational eigenstates of the M–He complexes (M=Cu,Ag,Au) in the electronic ground state are collected in Table IV, and the radial part of the corresponding wave functions are reported in Fig. 4. The rovibrational structure of all complexes is very simple and can be described in terms of the well-defined quantum numbers n (the number of nodes of the radial part of the wave function) and J (the rotational angular momentum). The rovibrational eigenstates have been computed using the Numerov algorithm as described by Cooley,[45] with an integration interval running from 0.0 to 50.0 Å, and adopting a step size of 0.01 Å. The accuracy of the results obtained with the CCSD(T) potentials has been double-checked with the grid method proposed by Tobin and Hinze,[46] adopting the same integration interval and step size. Calculations conducted with different integration intervals, step sizes, and algorithms ensure that the convergence on eigenvalues is well below 0.1 μhartree.

We considered the two natural isotopes of copper (^{63}Cu and ^{65}Cu) and the two natural isotopes of silver (^{107}Ag and ^{109}Ag), the single one for gold (^{197}Au), and the heavier isotope of helium (^{4}He). The metal atoms are much heavier than helium, and hence the reduced mass of M–He complex is very close to that of ^{4}He in all M–He complexes. This means that the changes in rovibrational structures observed for different M–He complexes are essentially due to the different features of the interaction potential. In fact, in the case of Cu–He, the change in the isotopic mass of copper has a very small effect on the properties of some eigenstates, with energy differences limited to 0.1 μhartree, and 0.01 Å on the expectation value of the M–He internuclear distance $\langle R \rangle$. In the case of Ag–He, the increase in the isotopic mass of the silver atom has a negligible effect on the energy of all the eigenstates and reduces just by 0.01 Å the average Ag–He distance in the two states with larger angular momentum (J=2,3).

For any given M–He complex (M=Cu,Ag,Au), the CCSD(T) and the CCSDT potentials support the same number of bound states. As expected, the eigenstates obtained with the CCSDT potentials are shifted at lower (i.e., larger and negative) energies as compared to CCSD(T) values. The shifts in the eigenvalues are limited to about 1 μhartree in Cu–He and Au–He, and they are even smaller in Ag–He (about 0.5 μhartree). Consistently, the probability distributions of the wave functions computed with the CCSDT potential are more concentrated at shorter M–He internuclear distances as compared to the corresponding CCSD(T) results. This effect produces relevant changes in $\langle R \rangle$ in Cu–He,

TABLE IV. Rovibrational bound states of the $M-$He complexes ($M=$Cu, Ag, Au). We report the properties of the heavier ($M-$He) isotopes only when they differ from the ones obtained for M-He; energies in μhartree; distances in Å.

Systems	Potential	n [a]	J [b]	E [c]	$\langle R \rangle$ [d]
^{63}Cu$-^4$He (^{65}Cu$-^4$He)	CCSD(T)	0	0	−5.6	6.46
		0	1	−4.3	6.63 (6.62)
		0	2	−1.8 (−1.9)	7.20 (7.19)
^{63}Cu$-^4$He (^{65}Cu$-^4$He)	CCSDT	0	0	−6.8	6.24 (6.23)
		0	1	−5.4 (−5.5)	6.36
		0	2	−2.8 (−2.9)	6.74 (6.73)
^{107}Ag$-^4$He (^{109}Ag$-^4$He)	CCSD(T)	0	0	−9.3	6.00
		0	1	−7.9	6.07
		0	2	−5.2	6.27 (6.26)
		0	3	−1.4	6.83 (6.82)
^{107}Ag$-^4$He (^{109}Ag$-^4$He)	CCSDT	0	0	−9.8	5.94
		0	1	−8.4	6.01
		0	2	−5.7	6.19
		0	3	−1.8	6.67 (6.66)
^{197}Au$-^4$He	CCSD(T)	0	0	−26.7	4.90
		0	1	−24.9	4.92
		0	2	−21.2	4.97
		0	3	−15.7	5.05
		0	4	−8.7	5.18
		0	5	−0.2	5.48
		1	0	−0.1	>10 [e]
^{197}Au$-^4$He	CCSDT	0	0	−28.0	4.87
		0	1	−26.1	4.89
		0	2	−22.4	4.93
		0	3	−16.9	5.01
		0	4	−9.7	5.13
		0	5	−1.1	5.42
		1	0	−0.1	>10 [e]

[a]Vibrational quantum number.
[b]Rotational angular momentum.
[c]Energy of the eigenstate.
[d]Expectation value for the $M-$He internuclear distance.
[e]See text for details.

from 0.2 to 0.5 Å, while in Ag–He and Au–He these variations are relevant only in the states with higher angular momentum.

The Cu–He potentials support three bound states, including two rotational and no vibrational excitations. The Cu–He distance undergoes large excursions during the vibrations in the complex, as appears clear in Fig. 4. In fact, the computed average Cu–He distance is much larger than the minimum of the PES, and $\langle R \rangle - R_{min}$ measures 1.8–2.6 Å depending on the state considered.

The Ag–He potentials support four bound states with just three rotational excitations. The wave functions are somewhat more localized around R_{min}, with $\langle R \rangle - R_{min}$ values comparable to the case of copper (from 1.4 to 2.2 Å).

The CCSD(T) and CCSDT potentials for Au–He are markedly deeper than Cu–He and Ag–He ones. As a result, these PES support five rotational excitations and also one vibrational excited state. The eigenstates with vibrational ei-genvalue $n=0$ are much more localized around R_{min} than observed in the other complexes, and the $\langle R \rangle - R_{min}$ difference increases from 0.8 to 1.4 Å as the rotational angular momentum goes from $J=0$ to $J=5$. Conversely, the wave functions of the {$n=1$, $J=0$} states are delocalized over a wide range of internuclear distances, including values much larger than we considered in *ab initio* computations. We did not report the computed $\langle R \rangle$ values in Table IV because they are critically dependent on very subtle features of the long-range tail of the Au–He interaction potential, and their accurate determination is not the main scope of the present investigation.

IV. CONCLUSIONS

In this work we presented an *ab initio* investigation of the ground state potential of three weakly interacting complexes: Cu–He, Ag–He, and Au–He. To the best of our
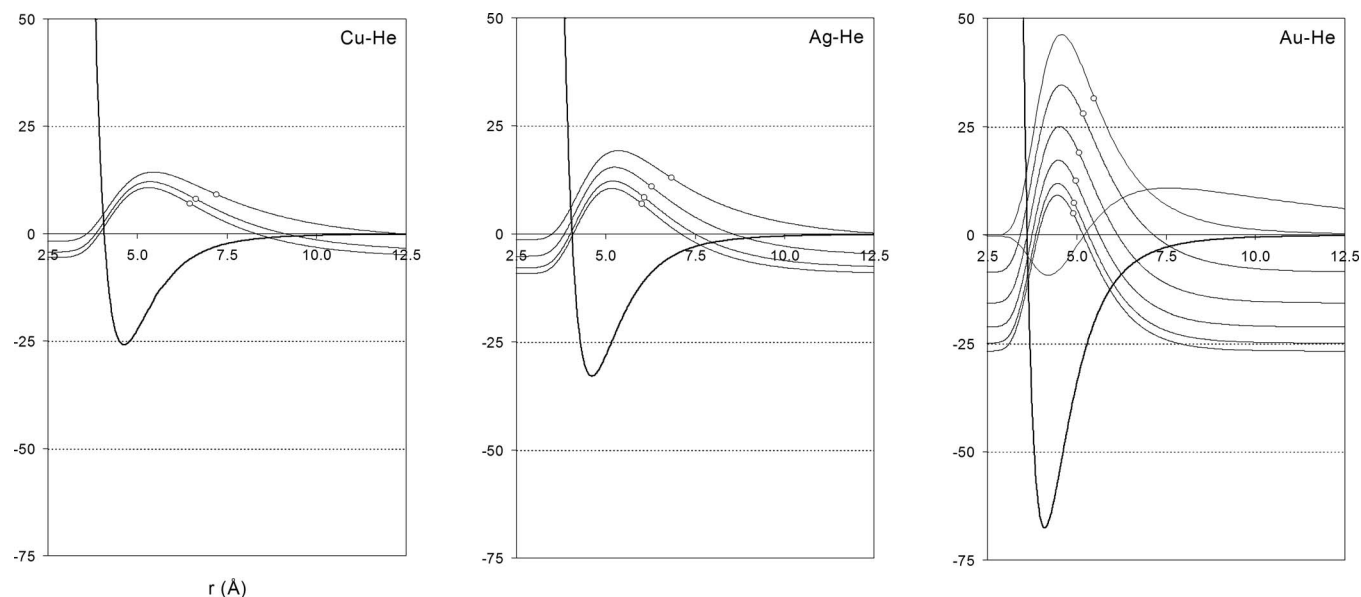
FIG. 4. CCSD(T) analytical ground state PES for the M−He complexes (M=Cu,Ag,Au), along with the radial part of the rovibrational nuclear wave functions. Each wave function is shifted at the corresponding eigenvalue. The empty circles are located at the expectation value of the M−He internuclear distance. All the wave functions reported are normalized to the same (arbitrary) value. The scale on the ordinates axis is referred to the interaction potentials (μhartree).

knowledge, there are no previous theoretical investigations on Cu–He and Au–He available in literature, and the earlier studies concerning Ag–He are based on a theoretical approach that does not provide very accurate results for this system.

We performed an extensive series of test computations to establish the computational approach, the theoretical level, and the basis set required to reach a high degree of accuracy in the determination of the interaction energy. First of all, it is necessary to include in correlated calculations at least the electrons of the outermost s, p, and d shells of the metal atom, along with the $1s^2$ electrons of helium. Second, the performance of the Møller–Plesset expansion at the MP4 level is quite poor on these systems. The MP4 method overestimates significantly the attractive well of the PES, and it underestimates the interaction energy in the region of the repulsive wall. On the other hand, the CCSD(T) level is very close to benchmark CCSDT results in a wide range of M−He distances. The CCSD(T) to CCSDT difference is limited to 1−2 μhartree in the attractive region of the PES, and increases very smoothly at decreasing M−He distances. Third, the interaction energy of the M−He systems in nearly converged when the following basis set is adopted: aug-cc-pVQZ for the metal atom, d-aug-cc-pVQZ for helium, plus the $3s3p2d$ set of bond functions placed at midway between M and He.

We computed the interaction energy of M−He complexes (M=Cu,Ag,Au) at the CCSD(T) level, adopting the cited basis set and including in correlated calculations the $1s^2$ for helium and the $(n-1)s^2(n-1)p^6(n-1)d^{10}ns^1$ electrons for the metal atoms, with n=4, 5, and 6 for Cu, Ag and Au, respectively. The UHF approach has been used to obtain the reference wave function, and the *core* electrons have been described with relativistic small core pseudopotentials: ([Ne]-PP) $3s^23p^63d^{10}4s^1$ for copper; ([Ar]$3d^{10}$-PP)

$4s^24p^64d^{10}5s^1$ for silver; and ([Kr]$4d^{10}4f^{14}$-PP) $5s^25p^65d^{10}6s^1$ for gold. For each complex we considered 30 internuclear distances to finely sample the attractive region of the potential and to get some information on the repulsive wall and the long-range tail. These results have been interpolated with quintic splines and define the analytical expression for the CCSD(T) interaction potentials.

We also computed the CCSD(T) and the CCSDT interaction energies in a limited set of internuclear distances, adopting the same theoretical scheme described above, and using a smaller basis set that recovers about 85% of the converged minimum interaction energy. The energy differences have been fitted on an exponential function to define an analytical CCSD(T) to CCSDT correction term for each M−He complex. The summation of these correction functions to the CCSD(T) PES defined the set of CCSDT interaction potentials.

The PES of Cu–He and Ag–He present the same features at varying M−He distance. The energy minimum is located at about 4.60 Å in both systems, and the PES becomes repulsive from 4.05 Å inward. The well depth of Ag–He measures 33 and 34 μhartree in the CCSD(T) and CCSDT potentials, respectively, and it is somewhat larger than found for the Cu–He complex, about 25 μhartree at CCSD(T) level and 28 μhartree considering the CCSDT PES. The Au–He interaction potential is much more attractive, about 70 μhartree, and shifted to shorter distances, with the minimum located at 4.1 Å and the repulsive wall starting at 3.6 Å.

As a first application of the two-body interaction potentials computed for Cu–He, Ag–He, and Au–He, we determined the rovibrational structure of the M−He dimers. In Cu–He and Ag–He the radial part of the ground state nuclear wave function is delocalized over several angstroms, and the expectation value of the internuclear distance $\langle R \rangle$ is nearly

2 Å larger than the position of the minimum of the well depth $R_{\min}$. The Cu–He and the Ag–He potentials support two and three rotational excitations, respectively, and no vibrational excited states. The ground state nuclear wave function of Au–He is much more localized than for Cu–He and Ag–He, and $\langle R \rangle$ is just 1 Å larger than $R_{\min}$. The Au–He PES supports rotational excitations up to $J=5$ and also the vibrational excited $\{n=1, \ J=0\}$ state.

Further investigations on these systems are currently under way in our laboratories, including Monte Carlo simulations on $M-\mathrm{He}_n$ aggregates ($M=\mathrm{Cu,Ag,Au}$) and *ab initio* computations of the $M-\mathrm{He}$ interaction potentials for the first excited states, to reproduce the results of spectroscopic experiments.

[1] J. P. Toennies and A. F. Vilesov, Angew. Chem., Int. Ed. **43**, 2622 (2004).

[2] C. Callegari, K. K. Lehmann, R. Schmied, and G. Scoles, J. Chem. Phys. **115**, 10090 (2001).

[3] M. Y. Choi, G. E. Douberly, T. M. Falconer, W. K. Lewis, C. M. Lindsay, J. M. Merritt, P. L. Stiles, and R. E. Miller, Int. Rev. Phys. Chem. **25**, 15 (2006).

[4] K. Szalewicz, Int. Rev. Phys. Chem. **27**, 273 (2008).

[5] S. Grebenev, J. P. Toennies, and A. F. Vilesov, Science **279**, 2083 (1998).

[6] F. Paesani, F. A. Gianturco, and K. B. Whaley, J. Chem. Phys. **115**, 10225 (2001).

[7] J. Tang, Y. Xu, A. R. W. McKellar, and W. Jäger, Science **297**, 2030 (2002).

[8] F. Paesani and K. B. Whaley, J. Chem. Phys. **121**, 4180 (2004).

[9] Y. Takahashi, K. Sano, T. Kinoshita, and T. Yabuzaki, Phys. Rev. Lett. **71**, 1035 (1993).

[10] J. L. Persson, Q. Hui, Z. J. Jakubek, M. Nakamura, and M. Takami, Phys. Rev. Lett. **76**, 1501 (1996).

[11] Z. J. Jakubek and M. Takami, Chem. Phys. Lett. **265**, 653 (1997).

[12] Z. J. Jakubek, Q. Hui, and M. Takami, Phys. Rev. Lett. **79**, 629 (1997).

[13] M. Mella, M. C. Colombo, and G. Morosi, J. Chem. Phys. **117**, 9695 (2002).

[14] A. Wada, T. Takayanagi, and M. Shiga, J. Chem. Phys. **119**, 5478 (2003).

[15] Y. Morikawi and N. Morita, Eur. Phys. J. D **5**, 53 (1999).

[16] J. Reho, U. Merker, M. R. Radcliff, K. K. Lehmann, and G. Scoles, J. Chem. Phys. **112**, 8409 (2000).

[17] M. Mella, G. Calderoni, and F. Cargnoni, J. Chem. Phys. **123**, 054328 (2005).

[18] A. Bartelt, J. D. Close, F. Federmann, N. Quaas, and J. P. Toennies, Phys. Rev. Lett. **77**, 3525 (1996).

[19] F. Federmann, K. Hoffmann, N. Quaas, and J. P. Toennies, Eur. Phys. J. D **9**, 11 (1999).

[20] F. Federmann, K. Hoffmann, N. Quaas, and J. D. Close, Phys. Rev. Lett. **83**, 2548 (1999).

[21] T. Diederich, J. Tiggesbäumker, and K.-H. Meiwes-Broer, J. Chem. Phys. **116**, 3263 (2002).

[22] A. Przystawik, P. Radcliffe, S. Göde, K.-H. Meiwes-Broer, and J. Tiggesbäumker, J. Phys. B **39**, S1183 (2006).

[23] A. Przystawik, P. Radcliffe, T. Diederich, T. Döppner, J. Tiggesbäumker, and K.-H. Meiwes-Broer, J. Chem. Phys. **126**, 184306 (2007).

[24] T. Döppner, T. Diederich, S. Göde, A. Przystawik, J. Tiggesbäumker, and K.-H. Meiwes-Broer, J. Chem. Phys. **126**, 244513 (2007).

[25] T. Döppner, T. Diederich, A. Przystawik, N. X. Truong, T. Fennel, J. Tiggesbäumker, and K.-H. Meiwes-Broer, Phys. Chem. Chem. Phys. **9**, 4639 (2007).

[26] V. Mozhayskiy, M. N. Slipchenko, V. K. Adamchuk, and A. F. Vilesov, J. Chem. Phys. **127**, 094701 (2007).

[27] E. Loginov and M. Drabbels, J. Phys. Chem. A **111**, 7504 (2007).

[28] D. Figgen, G. Rahut, M. Dolg, and H. Stoll, Chem. Phys. **311**, 227 (2005).

[29] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).

[30] R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981).

[31] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).

[32] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).

[33] J. Noga and R. J. Bartlett, J. Chem. Phys. **86**, 7041 (1987).

[34] G. E. Scuseria and H. F. Schaefer, Chem. Phys. Lett. **152**, 382 (1988).

[35] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.

[36] ACES II is a program product of the Quantum Theory Project, University of Florida. J. F. Stanton, J. Gauss, S. A. Perera, J. D. Watts, A. D. Yau, M. Nooijen, N. Oliphant, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K. K. Baeck, P. Rozyczko, H. Sekino, C. Huber, J. Pittner, W. Cencek, D. Taylor, and R. J. Bartlett. Integral packages included are VMOL (J. Almlöf and P. R. Taylor); VPROPS (P. Taylor); ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, and P. R. Taylor).

[37] K. A. Peterson and C. Puzzarini, Theor. Chem. Acc. **114**, 283 (2005).

[38] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **100**, 2975 (1994).

[39] F.-M. Tao, Z. Li, and Y.-K. Pan, Chem. Phys. Lett. **255**, 179 (1996).

[40] G. Calderoni, F. Cargnoni, A. Famulari, and M. Raimondi, J. Phys. Chem. A **106**, 5521 (2002).

[41] G. Calderoni, F. Cargnoni, and M. Raimondi, Chem. Phys. Lett. **370**, 233 (2003).

[42] R. J. Hinde, J. Phys. B **36**, 3119 (2003).

[43] R. J. Bartlett and M. Musial, Rev. Mod. Phys. **79**, 291 (2007).

[44] F. Ancilotto, P. B. Lerner, and M. W. Cole, J. Low Temp. Phys. **101**, 1123 (1995).

[45] J. W. Cooley, Math. Comput. **15**, 363 (1961).

[46] F. L. Tobin and J. Hinze, J. Chem. Phys. **63**, 1034 (1975).