

Long-range interactions of copper and silver atoms with hydrogen, helium, and rare-gas atoms

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(Received 14 July 2008; published 12 December 2008)

Dispersion interactions of the ground and resonantly excited states of Cu and Ag with a number of buffer gases are determined. The valence excitation spectrum was calculated by diagonalizing a semiempirical Hamiltonian in a large-dimension single-electron basis. The core made a significant contribution to the C_6 and C_8 dispersion coefficients for both copper and silver. Oscillator strengths and static scalar and tensor polarizabilities are given for some of the low-lying states.

DOI: [10.1103/PhysRevA.78.062710](https://doi.org/10.1103/PhysRevA.78.062710)

PACS number(s): 34.20.-b, 31.50.-x, 32.10.Dk, 32.70.Cs

I. INTRODUCTION

Although magneto-optical trap (MOT) cooling of atoms remains the preferred technique for the creation of degenerate quantum gases, the method is generally applicable to those atoms which can be optically pumped in a closed transition. Alkali-metal and rare-gas atoms are hence the most suitable for MOTs and optical traps. On the other hand, molecules do not have a closed optical transition and so cannot be cooled with a MOT. An alternative technique which has gained momentum is magnetic trapping and collisional cooling. Because the trapping is done solely with magnets, the atomic species must possess spin, and be paramagnetic, and because they are cooled in collision with a cold buffer gas (usually helium), they must have “good” collisional properties; i.e., cooling by elastic collisions must be overwhelming, compared with inelastic collisions. An example of inelastic collision is, for instance, one which would flip the spin of the particle and produce loss from the trap. The critical advantage of such a technique is that any paramagnetic atom or molecule could, in principle, be trapped and cooled.

In the cooling of paramagnetic atoms or molecules, the essential ingredient is the rate with which the good (elastic) collisions with the buffer gas atoms win over the bad (inelastic) collisions at cold temperatures. Detailed knowledge of the interactions between the paramagnetic atom or molecule and the He atom is paramount. Recent magnetic trapping and buffer gas cooling successes include CaH [1], rare-earth atoms [2], CaF [3], and NH [4]. In the NH-He cooling case, it was predicted that the ratio of elastic to inelastic collisions would exceed several tens of thousands [5].

Recently, transition-metal atoms, in particular copper and silver, have been trapped and cooled [6]. The trapping of large and dense samples of Cu and Ag atoms has been reported and large relaxation cross sections for Ag- ^3He collisions with anomalous temperature dependence have been observed. The trapping of Cu in the buffer gas trap, on the other hand, shows the normal inelastic rate dependence with temperature. At temperatures below 1 mK the kinetic energies of the particles are comparable in size to the magnitude of the

dispersion potential. A proper description of cold collisions for the Cu- ^3He and Ag- ^3He systems relies on a good understanding of the short- and long-range interatomic potentials. At the present time very little is known about these interactions [7] and it is desirable that this situation be rectified.

While an understanding of the collision dynamics with helium is the primary motivation for the present study, better knowledge of the long-range potentials of the noble metals with other gases is useful in a number of other contexts. These include the dynamics of impurity particles such as Cu and Ag in liquid helium [8–10]. Investigations of spin-flip transitions in the rare gases would complement recent research on hyperfine pressure broadening in the alkali-metal atoms [11]. The hydrides of the noble gases, e.g., CuH and AgH, have also been the subject of numerous investigations [12–23].

The actual calculation of the dispersion coefficients uses oscillator-strength sum rules [24–28]. For individual atoms with a simple structure this approach has advantages over other approaches such as Kohn-Sham density functional theory [29,30]. The sum-over-states approach automatically generates a representation of the excitation spectrum. Comparisons between model and experimental transition-rate data help facilitate a detailed error analysis. Further, the semiempirical model potential approach adopted has been shown to be capable of achieving accurate values for dispersion coefficients and polarizabilities [24,31].

II. METHOD OF CALCULATION

A. Wave functions and transition operators for Cu and Ag

The wave functions and transition operators computed in this paper for silver were computed by first diagonalizing the semiempirical Hamiltonian [24,32–35] in a large mixed Laguerre-type orbital (LTO) and Slater-type orbital (STO) basis set [24].

The initial step was to perform a Hartree-Fock (HF) calculation to define the core. In this case, calculations of the Ag $5s$ ground state were done in a STO basis [36]. The core

wave functions were then frozen, giving the working Hamiltonian for the valence electron:

$$H = -\frac{1}{2}\nabla^2 + V_{\text{dir}}(\mathbf{r}) + V_{\text{exc}}(\mathbf{r}) + V_p(\mathbf{r}). \quad (1)$$

The direct and exchange interactions of the valence electron with the HF core were calculated exactly. The ℓ -dependent polarization potential V_p was semiempirical in nature with the functional form

$$V_p(r) = -\sum_{\ell m} \frac{\alpha_d g_\ell^2(r)}{2r^4} |\ell m\rangle \langle \ell m|. \quad (2)$$

The coefficient α_d is the static dipole polarizability of the core, and $g_\ell^2(r) = 1 - \exp(-r^6/\rho_\ell^6)$ is a cutoff function designed to make the polarization potential finite at the origin. The cutoff parameters ρ_ℓ were tuned to reproduce the binding energies of the $5s$ ground state and the $5p$, $5d$, and $4f$ excited states. The dipole polarizability for Ag^+ , $\alpha_d = 8.829$ a.u., was taken from a random-phase-approximation (RPA) calculation [37]. The cutoff parameters for $\ell = 0 \rightarrow 3$ were $2.062a_0$, $2.325a_0$, $2.55a_0$, and $2.00a_0$, respectively. The energies of the states with $\ell \geq 1$ were assigned to the statistical average of their respective spin-orbit doublets. The Hamiltonian was diagonalized in a very large orbital basis with about 45 Laguerre-type orbitals for each ℓ value. The parameters for $\ell > 3$ were set to ρ_3 . The oscillator strengths (and other multipole expectation values) were computed with operators that included polarization corrections [24,33,38–40]. The quadrupole core polarizability was chosen as 49.9 a.u. [37], while the octupole polarizability was set to zero. The cutoff parameter for the polarization corrections to the transition operator was fixed at $2.25a_0$ (the average of ρ_0 , ρ_1 , ρ_2 , and ρ_3).

The excitation spectrum for Cu was determined with the methodology described above, and a model very much along these lines was used to describe positron and positronium interactions with neutral copper [41]. The only significant change from this previous model of copper was an increase in the number of LTOs for each ℓ from about 20 to 45.

This semiempirical approach to the calculation of oscillator strengths and polarizabilities has proved to be capable of giving results comparable in precision to high-quality *ab initio* calculations. A survey of dipole polarizabilities for the alkali-metal and alkaline-earth-metal atoms [24] gave polarizabilities that did not differ by more than 3% from polarizabilities and dispersion coefficients obtained with the best many-body perturbation theory calculations [42–44]. This high accuracy is possible because the asymptotic forms of the core-polarization operators are well founded in perturbation theory [38,39]. The use of effective operators simplifies the computations sufficiently so that close to exact solutions of the model Hamiltonian are possible. Finally, tuning the state energies to experimental energies enhances the accuracy of the long-range part of the wave function. A recent investigation of the polarizabilities of Mg^+ and Si^{3+} compared the present approach to the relativistic all-order single-double method wherein all single and double excitations from the reference Dirac-Fock configuration are included to all orders of perturbation theory [31]. The two methods gave

polarizabilities for the $3s$ and $3p$ states that agreed to better than 0.5%.

The transition arrays developed for the core utilized sum rules to determine the approximate oscillator-strength distribution [24,35]. The essential idea is to get an initial estimate of the oscillator-strength distribution from single-particle energies and expectation values of the HF wave functions. These are then adjusted using an energy shift to tune the core polarizabilities to values derived from experiment or reasonably accurate calculations. The end result is a pseudo-oscillator-strength distribution based on heuristic principles that satisfies the Thomas-Reiche-Kuhn sum rule and also gives the correct core dipole polarizability [24,35]. Application of this methodology to the determination of the rare-gas oscillator-strength distribution gave dispersion coefficients that were accurate to about 5% [35]. We assume a notional accuracy of 8% (i.e., about twice as large) for the derived oscillator strength distributions for Cu^+ and Ag^+ since the presence of low-lying excitations probably makes the procedure more susceptible to error.

B. Wave functions and transition operators for other atoms

The transition arrays for hydrogen and the rare gases are exactly the same as those in previous investigations of the dispersion interactions involving the low-lying states of the alkali-metal atoms and magnesium with these atoms [45,46]. The arrays for hydrogen and helium should be regarded as producing essentially exact polarizabilities and dispersion coefficients.

C. Calculation of the polarizabilities and dispersion constants

The polarizabilities and dispersion coefficients are evaluated by using sum rules over lists of oscillator strengths and reduced matrix elements [24–28]. The states included in the sums include all the physical and pseudostates resulting from the diagonalization of the LTO basis. The sum over the valence states implicitly includes the single electron continuum states.

The sum rules for the polarizabilities are well known [24–26,28] and do not need to be repeated in great detail here. Two of the better known results are the expression for the dipole polarizability α_d ,

$$\alpha_d = \sum_i \frac{f_{0i}}{\epsilon_{0i}^2}, \quad (3)$$

and the dipole-dipole dispersion parameter C_6 ,

$$C_6 = \frac{3}{2} \sum_{ij} \frac{f_{0i}f_{0j}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j} + \epsilon_{0i})}. \quad (4)$$

In these expressions, f_{0i} is the absorption oscillator strength and ϵ_{0i} is the excitation energy. These expressions assume the atom(s) are in a spherically symmetric state.

The actual sum rules for the dispersion parameters presented here are performed using the procedures outlined in [27]. These can be applied to atoms with any angular momentum, but reduce to the expression above involving sums

TABLE I. Theoretical and experimental energy levels (in hartrees) of some of the low-lying states of the Cu and Ag atoms. The energies are given relative to energy of the positively charged nd^{10} core. The experimental energies [47,48] for the doublet states are averages with the usual $(2J+1)$ weighting factors. The adjustable parameters in the polarization potential were tuned while giving the greatest weighting to the lowest state of each symmetry.

State	Theory	Experiment
Cu(4s)	-0.283942	-0.283939
Cu(4p)	-0.144038	-0.144056
Cu(5s)	-0.086265	-0.087392
Cu(5p)	-0.058843	-0.058933
Cu(4d)	-0.056404	-0.056399
Cu(6s)	-0.042689	-0.043143
Cu(5d)	-0.031563	-0.031564
Cu(4f)	-0.031353	-0.031391
Ag(5s)	-0.278474	-0.278421
Ag(5p)	-0.140986	-0.140976
Ag(6s)	-0.083393	-0.084521
Ag(6p)	-0.057320	-0.057745
Ag(5d)	-0.056300	-0.056272
Ag(4f)	-0.031432	-0.031447
Ag(6d)	-0.031442	-0.031425

over products of oscillator strengths [24–26,28] when both atoms are in spherically symmetric states. The oscillator-strength distributions for the core are inserted into the sum rules using identities developed in earlier work [24,27,60].

III. RESULTS

A. Energy levels

The binding energies of the low-lying states of neutral Cu and Ag are tabulated and compared with experiment in Table

I. The largest discrepancy between theory and experiment occurs for the Cu(5s) level and is 1.1×10^{-3} hartree. When the ρ_ℓ parameters of the polarization cutoff form factor are tuned to the lowest state of each symmetry, the tendency is for higher states of the same symmetry to be slightly underbound. This is evident in the comparisons in Table I.

B. Oscillator strengths

The absorption oscillator strength for a multipole transition [24,61] from $n_a \rightarrow n_b$, with an energy difference of $\Delta E_{n_b n_a} = E_{n_b} - E_{n_a}$, is defined as

$$f_{n_a n_b}^{(k)} = \frac{2|\langle \psi_{n_a}; L_a \| r^k \mathbf{C}^k(\hat{\mathbf{r}}) \| \psi_{n_b}; L_b \rangle|^2 \Delta E_{n_b n_a}}{(2k+1)(2L_a+1)}. \quad (5)$$

In this expression, L_a is the orbital angular momentum of the initial state while k is the polarity of the transition.

Table II lists the present oscillator strengths for a number of Cu and Ag transitions. The present oscillator strengths do not allow for splittings in the spin-orbit doublet. Data for the spin-orbit doublets from other calculations and experiment have been combined with the appropriate weighting factors to give a single f value. Results from three different classes of calculation are listed in Table II. The relativistic model potential (RMP) of Migdalek [49] is similar in philosophy to the present calculation since it is essentially a frozen-core calculation with a semiempirical polarization potential. However, a local exchange approximation is used and it is based on the Dirac as opposed to the Schrödinger equation. This method was refined in the core-polarization Dirac-Fock (CPDF) approach which incorporates exchange properly into the calculation [55]. There have been two many body perturbation theory (MBPT) calculations of transition rates for Cu-like and Ag-like atoms and ions by Johnson and co-workers [50,51].

The most important transition for the determination of the dispersion parameters is the resonant $ns \rightarrow np$ transition. The

TABLE II. Absorption oscillator strengths for various transitions of Cu and Ag. Experimental values are identified by the Expt. prefix before the citation. Theoretical values are identified by an acronym identifying the type of calculation.

Transition	Present	RMP [49]	MBPT [50,51]	Other
Cu				
$f_{4s \rightarrow 4p}^{(1)}$	0.7020	0.677	0.7129 [51]	0.659(6) Expt. [52], 0.659(80) Expt. [53]
$f_{4s \rightarrow 5p}^{(1)}$	0.00477			
$f_{4p \rightarrow 5s}^{(1)}$	0.1559	0.152		0.177 Expt. [54]
$f_{4p \rightarrow 4d}^{(1)}$	0.5661	0.552		0.51(6) Expt. [53]
$f_{4p \rightarrow 5d}^{(1)}$	0.1198	0.118		
Ag				
$f_{5s \rightarrow 5p}^{(1)}$	0.6970	0.661	0.6973 [51] 0.763 [50]	0.685 CPDF [55], 0.707(4) Expt. [56] 0.67(7) Expt. [57], 0.66(10) Expt. [58]
$f_{5s \rightarrow 6p}^{(1)}$	0.00461			
$f_{5p \rightarrow 6s}^{(1)}$	0.1650	0.163		0.167 CPDF [55], 0.147(20) Expt. [59]
$f_{5p \rightarrow 5d}^{(1)}$	0.5963	0.573	0.600	0.602 CPDF [55]
$f_{5p \rightarrow 6d}^{(1)}$	0.1174	0.115		

TABLE III. The static dipole, quadrupole, and octupole polarizabilities for the low-lying states of Cu and Ag. The tensor polarizability (for dipole excitations) of the Cu(4*p*) and Ag(5*p*) states are also given. The numbers in the square brackets denote powers of 10. All polarizabilities are given in atomic units.

State	α_1 (a.u.)	$\alpha_{1,2LL}$ (a.u.)	α_2 (a.u.)	α_3 (a.u.)
Cu(4 <i>s</i>)	41.65	0	332.4	5.580[3]
Cu(4 <i>p</i>)	138.9	-47.32	2.633[3]	1.790[5]
Ag(5 <i>s</i>)	46.17	0	391.6	7.194[4]
Ag(5 <i>p</i>)	155.2	-51.59	3.204[3]	4.898[5]

present copper 4*s* → 4*p* oscillator strength is 6% larger than the precise experiment of Carlsson *et al.* [52] and the older experiment of Kock and Richter [53]. The more sophisticated MBPT [51] calculation gives an oscillator strength of 0.7129, which is even larger than the present value of 0.7020.

It is surprising that there is a greater degree of conformity between theory and experiment for the resonant transition of the heavier silver atom. In this case the variation between the present calculation, the MBPT calculation of Chou and Johnson [51], and the CPDF calculation is less than 2%. However, the most recent MBPT calculation [50] gives an oscillator strength of 0.763, which seems anomalously large. The most precise experimental value for this oscillator strength, 0.707(4) [56], is closer to the calculations giving the smaller oscillator strengths.

C. Polarizabilities

The polarizabilities of the two lowest levels of Cu and Ag are listed in Table III. The dipole polarizabilities for the Cu and Ag ground states, respectively, were 41.65 a.u. and 46.17 a.u. The contribution from the resonant oscillator strength constitutes more than 98% of the total valence polarizability for both systems.

Polarizabilities derived from the RPA calculation are generally smaller than actual polarizabilities for the rare gases. The errors for the rare gases from Ne to Xe range from 12% to 1%, respectively [62]. It would seem reasonable to assume an error of about 10% in the polarizabilities of the Cu⁺ and Ag⁺ cores. Assuming an uncertainty of 8% in the Cu resonant oscillator strength (this is slightly larger than the difference between the present oscillator strength and experimental values) and an uncertainty of 10% in the core polarizability gives a total uncertainty of about 3.4 a.u. in the polarizability of the ground state. Assigning an uncertainty of 5% to the Ag resonant oscillator strength (again deduced by reference to the difference between the present oscillator strength and experimental values) and 10% to the core polarizability results in an overall Ag ground state uncertainty of 2.7 a.u.

The present Cu and Ag polarizabilities of 41.7(34) a.u. and 46.2(27) a.u., respectively, are compatible with the recommended values of 41.2(10) for Cu and 48.6(12) for Ag in the Handbook of Chemistry and Physics tabulation [63,64]. Some recent calculations based on density functional theory

TABLE IV. The dispersion coefficients (in a.u.) between the Cu(4*s*) and Ag(5*s*) states and the ground states of atomic hydrogen, helium, and the other rare gases. The numbers in the square brackets denote powers of 10.

System	C_6	C_8	C_{10}
Cu(4 <i>s</i>)-H	38.33	1.332[3]	5.519[4]
Cu(4 <i>s</i>)-He	16.25	477.1	1.718[4]
Cu(4 <i>s</i>)-Ne	32.89	1.030[3]	3.882[4]
Cu(4 <i>s</i>)-Ar	114.4	4.291[3]	1.864[5]
Cu(4 <i>s</i>)-Kr	165.3	6.691[3]	3.127[5]
Cu(4 <i>s</i>)-Xe	250.8	1.149[4]	6.035[5]
Ag(5 <i>s</i>)-H	45.55	1.657[3]	6.979[4]
Ag(5 <i>s</i>)-He	19.75	641.3	2.202[4]
Ag(5 <i>s</i>)-Ne	40.04	1.404[3]	5.019[4]
Ag(5 <i>s</i>)-Ar	137.9	5.500[3]	2.385[5]
Ag(5 <i>s</i>)-Kr	198.6	8.484[3]	3.979[5]
Ag(5 <i>s</i>)-Xe	299.8	1.437[4]	7.609[5]

TABLE V. The dispersion coefficients (in a.u.) between the Cu(4*p*) and Ag(5*p*) excited states and the ground states of atomic hydrogen, helium, and the other rare gases. The numbers in the square brackets denote powers of 10.

System		C_6	C_8	C_{10}
Cu(4 <i>p</i>)-H	Σ	138.9	1.785[4]	1.812[6]
Cu(4 <i>p</i>)-H	Π	78.53	1252	4.261[4]
Cu(4 <i>p</i>)-He	Σ	46.53	5.912[3]	5.916[5]
Cu(4 <i>p</i>)-He	Π	28.75	374.1	1.092[4]
Cu(4 <i>p</i>)-Ne	Σ	91.39	1.172[4]	1.206[6]
Cu(4 <i>p</i>)-Ne	Π	57.04	896.8	2.803[4]
Cu(4 <i>p</i>)-Ar	Σ	357.8	4.810[4]	5.143[6]
Cu(4 <i>p</i>)-Ar	Π	213.9	4359	1.637[5]
Cu(4 <i>p</i>)-Kr	Σ	535.6	7.307[4]	8.006[6]
Cu(4 <i>p</i>)-Kr	Π	315.8	7293	3.032[5]
Cu(4 <i>p</i>)-Xe	Σ	854.8	1.195[5]	1.369[7]
Cu(4 <i>p</i>)-Xe	Π	494.0	1.393[4]	6.669[5]
Ag(5 <i>p</i>)-H	Σ	152.0	2.099[4]	5.024[6]
Ag(5 <i>p</i>)-H	Π	89.04	1574	9.743[4]
Ag(5 <i>p</i>)-He	Σ	51.99	7.020[3]	1.753[6]
Ag(5 <i>p</i>)-He	Π	33.32	533.1	3.089[4]
Ag(5 <i>p</i>)-Ne	Σ	102.4	1.394[4]	3.486[6]
Ag(5 <i>p</i>)-Ne	Π	66.28	1267	6.938[4]
Ag(5 <i>p</i>)-Ar	Σ	396.6	5.672[4]	1.399[7]
Ag(5 <i>p</i>)-Ar	Π	245.8	5592	3.317[5]
Ag(5 <i>p</i>)-Kr	Σ	591.7	8.597[4]	2.112[7]
Ag(5 <i>p</i>)-Kr	Π	361.8	9156	5.609[5]
Ag(5 <i>p</i>)-Xe	Σ	940.0	1.402[5]	3.429[7]
Ag(5 <i>p</i>)-Xe	Π	563.2	1.703[4]	1.099[6]

have given $\alpha_d=39.5$ a.u. for Cu [29] and $\alpha_d=46.3$ a.u. for Ag [30]. Calculations of the polarizability that use a HF quality description of the valence electron significantly overestimate the polarizability; e.g., the compilation of Stiehler and Hinze [65] gives 77.2 a.u. for Cu.

IV. DISPERSION COEFFICIENTS

A. Dispersion coefficients of the ground state with helium

The dispersion coefficients of the Cu(4s) and Ag(5s) ground states with helium are listed in Table IV. It should be noted that a significant fraction of the C_n values for the ground state come from the core contribution. For example, the core comprises 42% of C_6 for Cu and 41% for Ag. Further, the contribution of the core to C_8 was 23% for Cu and 31% for Ag. These contributions are much larger than the core contribution to the dispersion coefficients involving the alkali-metal atoms [24,66].

The three major sources of error in C_6 arise from (a) the oscillator strength for the resonant transition, (b) the adopted dipole polarizability of core, and (c) the manner in which an oscillator strength distribution was derived from the core polarizability.

The overall degree of uncertainty in the resonant oscillator strength is between 5% and 8% for the two atoms. The errors in the polarizabilities of the Cu⁺ and Ag⁺ cores have been assigned to be about 10%. The error associated with the derived oscillator-strength distributions for the core was assigned to be $\pm 8\%$. Taking these three sources of error together, an overall uncertainty of $\pm 15\%$ is indicated for the

C_6 dispersion coefficients of the Cu and Ag ground states with helium.

B. Dispersion coefficients with other buffer gases

The dispersion coefficients of the Cu(4s) and Ag(5s) ground states with the ground states of hydrogen, helium, and the other rare gases are listed in Table IV for completeness purposes. The dispersion coefficients of the Cu(4p) and Ag(5p) excited states with the same list of atoms are found in Table V.

V. CONCLUSIONS

The dispersion coefficients of the copper and silver ground and resonant excited states with hydrogen, helium, and the rare-gas atoms are given. Static polarizabilities for these same copper and silver states are also given. The overall level of uncertainty in the dispersion coefficients for the copper and silver ground states is about 15%. This level of uncertainty is derived in equal parts from the description of the valence and core excitation spectrum. It would certainly be possible to get estimates of the dispersion parameters with improved precision. Existing technology could be used to get better estimates of the resonant transition rate and the core polarizability.

ACKNOWLEDGMENT

This work was supported in part by a National Science Foundation grant to ITAMP at the Harvard-Smithsonian Center for Astrophysics.

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