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Towards accurate all-electron quantum Monte Carlo calculations of transition-metal systems: Spectroscopy of the copper atom

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In this work we present all-electron fixed-node diffusion Monte Carlo (FN-DMC) calculations of the low-lying electronic states of the copper atom and its cation. The states considered are those which are the most relevant for the organometallic chemistry of copper-containing systems, namely, the ^2S, ^2D, and ^2P electronic states of Cu and the ^1S ground state of Cu^+. We systematically compare our FN-DMC results to CCSD(T) calculations using very large atomic-natural-orbital-type all-electron basis sets. The FN-DMC results presented in this work provide, to the best of our knowledge, the most accurate nonrelativistic all-electron correlation energies for the lowest-lying states of copper and its cation. To compare our results to experimental data we include the relativistic contributions for all states through numerical Dirac-Fock calculations, which for copper ($Z=29$) provide almost the entire relativistic effects. It is found that the fixed-node errors using Hartree-Fock nodes for the lowest transition energies of copper and the first ionization potential of the atom cancel out within statistical fluctuations. The overall accuracy achieved with quantum Monte Carlo for the nonrelativistic correlation energy (statistical fluctuations of about 1600 cm^{-1} and near cancelation of fixed-node errors) is good enough to reproduce the experimental spectrum when relativistic effects are included. These results illustrate that, despite the presence of the large statistical fluctuations associated with core electrons, accurate *all-electron* FN-DMC calculations for transition metals are nowadays feasible using extensive but accessible computer resources. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2011393]

I. INTRODUCTION

In recent years, quantum Monte Carlo (QMC) has been applied successfully to a number of electronic systems including atoms, molecules, liquids, and solids (see, e.g., Refs. 1–9 and the references in Ref. 10). The quality of the results obtained for total energies is in general very good; the accuracy achieved is comparable or even superior to that of standard high-quality *ab initio* methods (e.g., coupled cluster with large basis sets). However, the vast majority of systems studied so far involves only light elements of the first and second rows with small variations of the electronic density. Except for the innermost $1s$ electrons whose contribution is usually reproduced using effective core potentials (ECPs),[14] the energy scales present in these systems are quite restricted and Monte Carlo simulations are found to converge even for very large systems containing hundreds of electrons (e.g., up to 984 valence electrons are treated in Ref. 9). In contrast, much less has been done for the description of complex systems where the electronic density structure is more intricate. A prototypical example of such complexity is found in transition-metal systems. From a general perspective, the physicochemical and spectroscopic properties of metal-containing molecules are extremely difficult to describe accurately with the available electronic structure methods and this is one of the key issues of modern computational quantum chemistry. As is well known, this difficulty arises from the electronic complexity involved when many electrons are localized in a small spatial region ($3d$ or $4d$ shell of the transition-metal family). It is crucial to emphasize that for a wide variety of cases the understanding of the basic processes at work in the metal-containing systems requires quantitatively a high degree of accuracy on the transition energies between the low-lying electronic states.

Up to date only a limited number of quantum Monte Carlo studies have addressed this important problem.[11–26] To our knowledge all QMC applications involving transition-metal atoms, except for the work of Belohorec *et al.*[15] (see also Rothstein[16,17]), have used effective core potentials to reproduce the effect of the innermost electrons. The major motivation for introducing pseudopotentials is to remove from the simulation the large energy and small length scales associated with the chemically inactive core electrons. Spectroscopic properties calculated as differences of total energies are thus much less noisy (the large statistical fluctuations coming from the core electrons have been removed) and a much larger time step can be used for propagating valence electrons. Both aspects lead to very important gains in computer time compared to all-electron calculations. However, the price to pay for these advantages is the introduction of two additional systematic errors besides the usual fixed-node error common to all-electron and pseudopotential

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calculations. The first error is associated with the pseudopotential itself and the second one is the so-called localization error resulting from the localization of the nonlocal ECP operator by projection over an approximate trial wave function. Flad and Dolg[20] have presented a detailed analysis of the accuracy of pseudopotential-based QMC calculations by computing atomic ionization and excitations energies for the first-row transition metals Sc,V,Ti, and Cr and by systematically comparing the results to configuration-interaction (CI) and coupled-cluster (CC) calculations using the same pseudopotentials and very large basis sets. When using small-core (Neon-core) pseudopotentials they estimate the error due to the nonlocal pseudopotential for these systems to be at most 0.1 eV. The localization and fixed-node errors are found to be quite dependent on the quantity evaluated (ionization or excitation energies), on the occupation of the 3*d* and 4*s* shells, and on the nature of the trial wave function used [with or without Jastrow for the explicitly correlated part of the wave function, using multiconfiguration self-consistent-field (MCSCF) or restricted Hartree-Fock (RHF) forms for the determinantal part]. Although it is not easy to evaluate the relative importance of the fixed-node and localization error (these errors are difficult to separate), the results presented by Flad and Dolg seem to indicate a localization error on the differences of energies lying between 0.1 and 0.5 eV. Note that in an early study of the low-lying electronic states of the iron atom Mitáš[19] obtained similar results, although for the Fe atom the localization error appears to be smaller than for the systems studied by Flad and Dolg. Finally, note that in the recent years some ECP-QMC calculations on molecular systems have been presented: dissociation energy and energy splittings of the low-lying states of TiC,[24] binding energies of TiO and MnO,[25] relative energies of various clusters such as $CuSi_4$, $CuSi_6$,[21] and Cr_2CO,[23] singlet-triplet gap for $Ti@Si_{12}$,[22] and dissociation energies of transition-metal carbonyls.[26]

In this work our purpose is to show that accurate all-electron quantum Monte Carlo calculations for a transition-metal atom such as copper can be performed despite the presence of large fluctuations associated with core electrons. In contrast with the early works of Belohorec *et al.*[15] and Rothstein,[16,17] we use here an accurate fixed-node diffusion Monte Carlo scheme and not a variational Monte Carlo (VMC) approach biased by the choice of a particular trial wave function for each electronic state. Using all-electron FN-DMC calculations allows to avoid the limitations of the pseudopotential approach discussed above and, in particular, the delicate issue of estimating the systematic errors. Our results for the electronic transitions $Cu(^2S)\rightarrow Cu(^2D)$, $Cu(^2S)\rightarrow Cu(^2P)$, and $Cu(^2S)\rightarrow Cu^+(^1S)$ (ionization potential) show that a statistical accuracy of about 0.15 eV can be achieved. Within this error bar of 0.15 eV a full agreement between the transition energies computed at the fixed-node DMC level and the experimental data is obtained. In particular, the systematic fixed-node error associated with both initial and final electronic states is found to cancel within statistical fluctuations. Of course, to compare our results with the experimental spectrum the relativistic effects need to be taken into account. These effects include both scalar (Darwin and mass velocity) and *J*-dependent spin-orbit contributions. For copper ($Z=29$) they are known to be adequately reproduced at the self-consistent-field level and can be directly added on top of the nonrelativistic correlation energies (additivity of relativistic and correlation effects). Finally, since standard highly correlated *ab initio* techniques can accurately reproduce the transition energies of Cu, we systematically compare our QMC results with all-electron CCSD(T) calculations using large optimized basis sets.

The organization of this paper is as follows. In Sec. II we present the computational methods used in this work [QMC, relativistic Dirac-Fock, and *ab initio* CCSD(T) approaches]. In particular, a detailed presentation of the QMC strategy employed to get stable and accurate all-electron calculations is given. In Sec. III we discuss our results and, finally, some conclusions are presented in Sec. IV.

II. COMPUTATIONAL METHODS

As pointed out in the Introduction we shall use the fact that the total energy for a given electronic state can be decomposed as

$$E_{i,J}^{\mathrm{tot}} = E_i^{\mathrm{scal.rel}}(\mathrm{DF}) + E_{i,J}^{\mathrm{SO}}(\mathrm{DF}) + E_i^{\mathrm{corr.nonrel}} + O(\epsilon^{\mathrm{rel-corr}}), \tag{1}$$

where *i* denotes the *L*, and *S* quantum numbers (^2S, ^2D, ^2P, and ^1S in our case) and *J* the total angular momentum. The first two terms in the right-hand side of the equation correspond to the main relativistic effects computed at the Dirac-Fock (DF) level (scalar effects representing the Darwin and mass-velocity terms plus the spin-orbit ones); the third term is the exact nonrelativistic correlation energy. Such an approximation is reasonable since it is known that the coupling between relativistic and correlation effects is rather small for $Z=29$. In what follows, we shall compute the total relativistic effects, $E_{i,J}^{\mathrm{rel}}(\mathrm{DF})$, via a Dirac-Fock description (see Sec. II B) and the nonrelativistic correlation energies using either QMC (Sec. II A) or CCSD(T) (Sec. II C). Our final working formula becomes

$$E_{i,J}^{\mathrm{tot}} \simeq E_{i,J}^{\mathrm{rel}}(\mathrm{DF}) + [E_i^{\mathrm{nonrel}}(\mathrm{exact}) - E_i^{\mathrm{nonrel}}(\mathrm{HF})]. \tag{2}$$

A. Quantum Monte Carlo

QMC methods are powerful stochastic approaches for solving the Schrödinger equation. In this work we shall use the FN-DMC method, the most commonly used variant of QMC approaches for treating complex electronic systems. Since several excellent presentations of the diffusion Monte Carlo method have been published (see, e.g., Refs. 27, 28, and 10) we shall not enter here into the details of the algorithm. We shall restrict the presentation of DMC to the sole equations useful for the understanding of our practical implementation of the method to high-*Z* systems such as copper and its cation.

In the fixed-node DMC approach a population of "walkers" is introduced. A walker is defined as the set of the spatial coordinates of the *N* electrons of the system, $\mathbf{R}=(\mathbf{r}_1,\ldots,\mathbf{r}_N)$. At each step of the simulation the walkers are propagated using a Langevin-type move,

$$\mathbf{R}_{\text{new}} = \mathbf{R}_{\text{old}} + \mathbf{F}[\mathbf{R}_{\text{old}}]\tau + \sqrt{\tau}\eta, \tag{3}$$

where τ is the elementary time step, $\mathbf{F}$ the drift vector given by $\mathbf{F}(\mathbf{R}) = \nabla\psi_T(\mathbf{R})/\psi_T(\mathbf{R})$, where ψ_T is some optimized trial wave function, and η a $3N$-dimensional Gaussian random vector ($3N$ *independent* normal Gaussian components).

To reduce the finite time step error, a Metropolis step is performed and the preceding Langevin move is accepted with probability

$$q = \min\left[1, \frac{\psi_T(\mathbf{R}_{\text{new}})^2 p(\mathbf{R}_{\text{new}} \to \mathbf{R}_{\text{old}}, \tau)}{\psi_T(\mathbf{R}_{\text{old}})^2 p(\mathbf{R}_{\text{old}} \to \mathbf{R}_{\text{new}}, \tau)}\right], \tag{4}$$

where $p(\mathbf{R} \to \mathbf{R}', \tau)$ is the Gaussian transition probability associated with Eq. (3), $p(\mathbf{R} \to \mathbf{R}', \tau) \sim \exp[-(\mathbf{R}' - \mathbf{R} - \mathbf{F}(\mathbf{R})\tau)^2/2\tau]$. Finally, the last step consists in simulating a birth/death (branching) process by deleting or duplicating (a certain number of times) each walker according to the local branching weight given by

$$W(\mathbf{R}_{\text{old}}, \mathbf{R}_{\text{new}}, \tau) = e^{-\tau[(E_L(\mathbf{R}_{\text{old}}) + E_L(\mathbf{R}_{\text{new}}))/2 - E_T]}, \tag{5}$$

where $E_L(\mathbf{R})$ is the local energy, $E_L(\mathbf{R}) = H\psi_T(\mathbf{R})/\psi_T(\mathbf{R})$, and E_T some reference energy.

In the long-time limit the walkers are distributed according to the DMC density

$$\Pi_{\text{DMC}}(\mathbf{R}) \sim \phi_0(\mathbf{R})\psi_T(\mathbf{R}), \tag{6}$$

where ϕ_0 represents the exact unknown ground-state wave function. The exact energy is obtained by averaging the local energy over the stationary DMC population.

Four different types of error are present in the fixed-node diffusion Monte Carlo algorithm. The most fundamental one is the fixed-node error related to the fact that during the simulation the walkers are trapped into the nodal pockets delimited by the nodal hypersurfaces of ψ_T (the nodes act as infinitely repulsive barriers). The *positive* DMC density actually recovered by implementing the DMC algorithm is not the true density $\phi_0\psi_T$ of Eq. (6) (which actually has no reason to have a constant sign) but some approximate positive density associated with the fixed-node wave function ϕ_0^{FN}, the solution of the Schrödinger equation having the same nodes as the trial wave function (additional boundary conditions with respect to the standard case). It can be shown that the fixed-node approach is variational[29] and various studies have illustrated that the corresponding error is in general small (a few percent of the correlation energy, depending on the quality of the nodes). A second source of error is the short-time error associated with the use of noninfinitesimal values for the time step. This error appears through the implementation of Eqs. (3) and (5) and also because of the presence of unwanted crossings of the nodes (walkers can "jump" over the nodes and the fixed-node constraint is not exactly fulfilled). This error is easily controlled by performing different calculations with different time steps and by extrapolating the results to zero time step. A third source of error is the so-called population control error.[30] This error results from the fact that some sort of population control is needed to keep the average number of walkers roughly constant (nothing preventing the population from exploding or collapsing). A usual solution to this problem consists in smoothly adjusting during the simulation the reference energy E_T appearing in Eq. (5) to impose a stabilized population. Finally, the last error is the Monte Carlo error itself. As is well-known this error is inversely proportional to the square root of the number of independent configurations used to compute averages.

A central aspect of fixed-node DMC calculations is the choice of the trial wave function, ψ_T. The closer the trial wave function is to the exact unknown wave function, the smaller the various errors described above are. Here, we have chosen for the trial wave function a standard form used in most studies, namely,

$$\psi_T(\mathbf{R}) = \exp\left[\sum_{\langle i,j\rangle} U(r_i, r_j, r_{ij})\right] D^{\uparrow}(\mathbf{R}) D^{\downarrow}(\mathbf{R}), \tag{7}$$

where $D^{\sigma}(\mathbf{R})(\sigma = \uparrow \text{ or } \downarrow)$ are SCF determinants made of one-particle space orbitals and $\exp[\Sigma_{\langle i,j\rangle} U(r_i, r_j, r_{ij})]$ is an explicitly correlated prefactor (Jastrow term) taking into account various n-body effects (electron-electron cusp, electron-electron-nucleus three-body term, etc.).

In this work we have done extensive FN-DMC simulations for the ^2S, ^2D, and ^2P electronic states of Cu and the ^1S ground state of Cu$^+$. The time step used is small enough to achieve a very high acceptance rate [average value of the probability q of Eq. (4)], to avoid large fluctuations of the branching weight [Eq. (5)] and to get a very small amount of nodal crossings. For the four electronic states considered here we have taken $\tau = 0.000\,02$ a.u. in our production runs. We have checked that using a smaller time step of $\tau = 0.000\,01$ a.u. does not change our results within statistical uncertainties. In the case of the ^1S ground state of Cu$^+$ the acceptance rate obtained is $\langle q\rangle \simeq 0.9956$ and the frequency of nodal crossing is about 0.000 14; similar values have been obtained for the other electronic states. Our time step is particularly small compared to values employed elsewhere. In the all-electron variational Monte Carlo study of Belohorec *et al.* and Rothstein on the CuH molecule,[15–17] the smallest time step used for moving the innermost electrons was 0.000 16 a.u. In the work of Flad and Dolg[20] based on the use of pseudopotentials $\tau = 0.002\,50$ for Sc and Ti and $\tau = 0.002\,00$ for V and Cr. Note the existence of two orders of magnitude between our all-electron time step and the typical time step used in the QMC calculations with pseudopotentials. To get energy estimators correctly converged a sufficiently large number of Monte Carlo steps for each walker have to be done. This is an essential condition to have a correct sampling of the entire configuration space. In our simulations a number of steps of about 3×10^6 has been performed, corresponding to random walks of length 60 a.u. We have checked that such a length is sufficient by making several simulations starting from various initial configurations and using independent series of random numbers. No systematic drift in the distribution of results has been observed, as it could occur when there is some lack of ergodization. With the trial wave functions and time step used here, the branching weights [Eq. (5)] are found to vary very little during the simulation. For the ^1S ground state of Cu$^+$ we have obtained $W_{\min} \sim 0.90$ and $W_{\max} \sim 1.03$. With such values the population control error is rapidly negligible when

TABLE I. Minimum of the local energy and maximum of the branching weight W [Eq. (5)] in a FN-DMC calculation for the ^1S state of Cu^+ as a function of the type of orbitals used for constructing the SCF wave function [Slater-type orbitals (STOs) or Gaussian-type orbitals (GTOs)]. The average energy and the variance of the local energy [$\sigma^2 = \langle (E_L - \langle E_L \rangle)^2 \rangle$] are also given. [Ne] denotes the Neon-core configuration: $1s^2 2s^2 2p^6$. The FN-DMC calculation has been done with an average of 100 walkers and 4×10^6 Monte Carlo steps per walker.

	STO:[Ne]/GTO: $3s^2 3p^6 3d^{10}$	STO:[Ne] $3s^2$/GTO: $3p^6 3d^{10}$	STO:[Ne] $3s^2 3p^6 3d^{10}$
E_L(min)	−66 005.86	−5126.96	−3127.95
W(max)	1.902	1.037	1.0153
$\langle E_L \rangle$	−1640.15(4)	−1640.15(3)	−1640.13(3)
σ^2	482(27)	419(1)	416(1)

using a not so large population of walkers. Here, the population sizes have been maintained around 100 walkers and no significant changes in the results (within statistical uncertainties) have been observed with larger populations. Finally, the values presented here have been obtained by performing parallel computations using 32–64 processors. The total statistics for each electronic calculation is about 32 (number of processors) × 100 (population size) $\times 3 \times 10^6$ (Monte Carlo steps per walker), that is, a total of about 10^{10} configurations for averages. Using a single Power4 processor, each calculation presented in this work has a computational cost of about 2000-h CPU.

Finally, let us now comment in more detail the choice of the trial wave function. We have found that to get well-behaved convergence of the energy estimators as a function of the simulation time it is essential to describe accurately the wave function at very short electron-nucleus distances. For example, using a large all-electron optimized atomic natural orbital Gaussian basis set[31] ($20s15p10d$) with the largest s exponent equal to 5 430 320.9 is not sufficient for getting stabilized DMC simulations. Convergence properties are hindered by occurrence of rare events associated with very large negative local energies (no compensation between the kinetic and the large Coulombic $-Z/r$ terms). To avoid this problem we have employed Hartree-Fock (HF) orbitals expressed in a Slater basis set. For the ^2S of Cu we have used the HF solution presented by Bunge *et al.*,[32] and for the ^2D state of Cu and the ^1S ground-state of Cu^+ the solutions proposed by Clementi and Roetti.[33] In the case of the ^2P electronic state of Cu for which we have not been able to find a Hartree-Fock solution in the literature, a hybrid Gaussian/Slater representation for the wave function has been used. The innermost orbitals belonging to the Neon core and the $3s$ valence orbital have been chosen to be the Slater orbitals of the ^2S ground state of the copper atom, the remaining valence orbitals $3p$, $3d$, and $4p$ being the Gaussian orbitals of the ^2P electronic state obtained using the MOLPRO2002.6 program[34] with the ($20s15p10d$) atomic natural orbital (ANO) basis set developed by Bauschlicher, Jr.[31] Note that replacing the Gaussian $3s$ orbital of the ^2P state by the Slater $3s$ orbital of the ^2S ground state is harmless here since the global shape of both orbitals is almost identical. However, because the $3s$ orbital has a nonvanishing probability at the nucleus, such a replacement has a huge impact on the range of values taken by the local energy and, thus, on the convergence properties of the simulation. To illustrate this important point we present in Table I the minimal value taken by the local energy and the maximal value of the branching weight during a DMC simulation as well as the estimates of the total energy and of the variance of the local energy, $\sigma^2 = \langle (E_L - \langle E_L \rangle)^2 \rangle$. These data are presented for the ^1S state of Cu^+ and not for the ^2P state of Cu since in the first case pure Slater simulations are possible.

As seen in the table the data illustrate very clearly the importance of correctly describing the short electron-nucleus behavior not only of the orbitals of the Neon core but also of the $3s$ valence orbital. In particular, let us emphasize that in spite that the $1s$, $2s$, and $2p$ orbitals are taken from the HF-STO atomic solution the simulation still produces rare events associated with too low local energies, almost 13 times smaller than the lowest local energy for the simulation where the $3s$ orbital is also included in the Slater part. The presence of these rare events is responsible for the large value of the maximum of the branching weight (1.902 instead of 1.037 and 1.015) and also of the very large fluctuations on the variance of the local energy. Let us remark that, although the final energy average obtained with the Slater-type orbital (STO) Neon-core only (first column of Table I) seems satisfactory here, we have observed a poor reproducibility of such a calculation when using different initial conditions and different random numbers. We insist that having local energies with a not too large magnitude is a prerequisite for getting well-behaved DMC simulations. Finally, using a variational Monte Carlo calculation we have checked that the energy of the pure Gaussian solution given by MOLPRO and the energy of our Gaussian/Slater wave function almost coincide within statistical uncertainties, although an accurate comparison is difficult due to the large fluctuations associated with the Gaussian solution.

Regarding the Jastrow part we have tried two different forms. Our first choice is a standard "minimal" form taking care of the electron-electron cusp and a simple one-body electron-nucleus term:

$$U(r_i, r_j, r_{ij}) = a r_{ij}/(1 + b r_{ij}) - p(r_i + r_j), \tag{8}$$

where parameters a and b can take two different values depending on the pairs of electrons considered (parallel or antiparallel). We have imposed the following exact cusp conditions: $a=0.5$ for antiparallel and $a=0.25$ for parallel spins.[29] The three other parameters: b_{parallel}, $b_{\text{antiparallel}}$, and p, have been used as variational parameters. The second form considered here is a more sophisticated expression including a systematic expansion of $U(r_i, r_j, r_{ij})$ in powers of x_{ij}

TABLE II. All-electron nonrelativistic total energies and correlation energies of the low-lying states of copper and its cation using SCF, CCSD(T), and FN-DMC. (Basis set for CCSD(T): Fully uncontracted $22s17p11d7f5g2h2i$ augmented from ANO basis given in Ref. 31.) Energies in a.u. Statistical errors on the last digit in parentheses, e.g., −1640.411(5) means −1640.411±0.005.

	$E_{\rm SCF}^{\rm nonrel}$	$E_{\rm CCSD(T)}^{\rm nonrel}$	$E_{\rm CCSD(T)}^{\rm corr.nonrel}$	$E_{\rm FN\text{-}DMC}^{\rm nonrel}$	$E_{\rm FN\text{-}DMC}^{\rm corr.nonrel}$
Cu(^2S)	−1638.9637	−1640.3971	−1.4334	−1640.411(5)	−1.447(5)
Cu(^2D)	−1638.9528	−1640.3276	−1.3748	−1640.342(4)	−1.392(4)
Cu(^2P)	−1638.8508	−1640.2619	−1.4111	−1640.273(5)	−1.422(5)
Cu$^+$(^1S)	−1638.7276	−1640.1204	−1.3928	−1640.137(6)	−1.409(6)

$\equiv r_{ij}/(1+br_{ij})$ and $x_i \equiv r_i/(1+cr_i)$ as well as some terms introducing the explicit couplings between the variables x_{ij} and x_i (electron-electron-nucleus three-body terms). This last form is very similar to the expression proposed in Ref. 35. The variational parameters entering in the Jastrow terms have been optimized using the correlated method of Umrigar *et al.*,[36] a standard approach based on the minimization of the weighted variance of the local energy over a set of fixed configurations.

Quite surprisingly, for the various electronic states considered here we have not been able to get *reliable* optimized parameters for the sophisticated form. Optimal parameters obtained from our minimization procedure have systematically led to unsufficiently converged DMC simulations, at least with the number of Monte Carlo steps performed in our simulations. We have found no improvement with the optimized parameters obtained when increasing the number of fixed configurations used in the optimization step (up to 10 000) or when changing the set of fixed configurations. In contrast, the optimized minimal form [Eq. (8)] has systematically led to reliable FN-DMC simulations and, therefore, it is this simple form that has been employed in this work. We let for future work a precise understanding of the origin of the difficulties observed when optimizing our sophisticated trial wave function for these high-Z systems. Finally, let us mention that the typical values of the variance of the local energy for the wave functions used here (simple optimized Jastrow+SCF part) are about $\sigma^2 \sim 100-110$.

B. Relativistic effects

Ab initio relativistic Dirac-Fock energies have been obtained with the formalism and code developed by Lindgren and Rosén[37] Calculations are done using a logarithmic numerical grid. Thanks to the spherical symmetry of atoms, the algorithm reduces to a one-dimensional case and, thus, the Dirac-Fock limit is easily reached. Note that for the systems treated here the Breit term is small[38] and is not included in our calculations. Note also that the spin-orbit splitting is quite well reproduced at the Dirac-Fock level.

C. *Ab initio* correlation treatment

Ab initio correlation energies have been computed with the all-electron optimized atomic natural orbital basis set developed by Bauschlicher, Jr.[3] The original $(20s15p10d6f4g)$ ANO basis has been augmented with a set of even-tempered $2s2p1d1f1g2h2i$ orbitals, so that we end up with a $(22s17p11d7f5g2h2i)$ fully uncontracted basis set (available upon request). The calculations have been made with the MOLPRO2002.6 code.[34] Hartree-Fock references have been used to perform restricted open-shell coupled cluster calculations at the CCSD(T) level with all the orbitals active. Using this rather large basis set, the CCSD(T) space contains around 2.6×10^6 configuration state functions (CSFs) for the 29-electron Cu doublet states. Each CCSD(T) calculation takes less than 130 mins on a single Power4 processor with a 256-MB random access memory (RAM) requirement.

III. RESULTS AND DISCUSSION

In Table II we present the total energies calculated at the nonrelativistic level using SCF, CCSD(T), and fixed-node DMC approaches for the first three electronic states ^2S, ^2D and ^2P of the copper atom as well as the ground state ^1S of the copper ion. We explicitly show the correlation energy for each state with both correlated methods. It is seen that the FN-DMC energies are systematically lower than the corresponding CCSD(T) values. Given the fact that the fixed-node method is variational,[29] we conclude that the DMC approach recovers a larger fraction of the total correlation energy. Note that the statistical errors on the DMC energies are small enough to validate such a conclusion. To the best of our knowledge, the values presented in Table II provide the most accurate all-electron nonrelativistic energies available for the lowest-lying states of copper and its cation.

Getting very accurate total energies is certainly desirable but, for practical purposes, we are much more interested in obtaining high-quality *energy differences*. In Table III SCF, CCSD(T), and QMC energy differences are shown. At the SCF level the $^2S \rightarrow {}^2D$ transition is very badly reproduced (2392 cm^{-1} instead of about 15 000 cm^{-1} with correlation). Such a result is expected since this transition implies a change in the occupation of the $3d$ shell, a situation where the electronic correlation plays a major role. For the two other transitions where the number of $3d$ electrons remains constant, the SCF errors are about 6000 cm^{-1} for the ^2S

TABLE III. Nonrelativistic transition energies between the low-lying states of copper computed at the SCF, CCSD(T), and FN-DMC levels. Energies in wave numbers. Statistical errors on the last digit in parentheses for DMC data.

	$\Delta E_{\rm SCF}^{\rm nonrel}$	$\Delta E_{\rm CCSD(T)}^{\rm nonrel}$	$\Delta E_{\rm FN\text{-}DMC}^{\rm nonrel}$
Cu $^2S \rightarrow {}^2D$	2 392	15 254	15 144(1 405)
Cu $^2S \rightarrow {}^2P$	24 779	29 673	30 288(1 552)
Cu $^2S \rightarrow$ Cu$^+$ ^1S (IP)	51 818	60 729	60 136(1 714)

TABLE IV. Numerical Dirac-Fock total energies (a.u.) for the low-lying states of copper. Spin-orbit splittings within each multiplet in wave numbers.

Configuration	J	E_J(DF)	SO splitting (cm^{-1})
$^2S(3d^{10}4s^1)$	1/2	−1653.461 99	
$^2D(3d^9 4s^2)$	3/2	−1653.458 48	
	5/2	−1653.469 91	2509
$^2P(3d^{10}4p^1)$	1/2	−1653.345 19	
	3/2	−1653.344 36	181
$^1S(3d^{10})$	0	−1653.220 67	

$\rightarrow {}^2P$ transition (the correlated value being close to 30 000 cm^{-1}) and 10 000 cm^{-1} for the $^2S \rightarrow \mathrm{Cu}^+ \ {}^1S$ transition (correlated value of about 61 000 cm^{-1}). Although much smaller than in the previous case the magnitude of these errors illustrates the importance of correlation effects on such transitions. Note that in the case of the $^2S \rightarrow {}^2D$ transition our result of 15 254 cm^{-1} is quite close to the QCISD(T) value of 14 921 cm^{-1} presented by Raghavachari and Trucks in Ref. 39. As seen in Table III no significant differences between the transition energies calculated with CCSD(T) and FN-DMC are observed within statistical error bars, the typical DMC error being about 1600 cm^{-1}.

The fact that CCSD(T) and FN-DMC give similar transition energies is an important result which deserves some comment. Clearly, some cancelation of errors must be at work in both approaches. For CCSD(T) numerical experience has shown that such cancelation is indeed observed when—like in the present case—the two wave functions share some common structure (several occupied orbitals having almost the same shape) and when a common basis set is used for the calculations. For QMC the situation is different. Each DMC calculation is associated with a fixed-node error depending solely on the quality of the nodal structure employed for the state under consideration. Clearly, it is difficult to know whether the nodal errors associated with the two states involved in a transition will compensate or not. The results obtained here for the copper atom show that using the Hartree-Fock nodes for both states leads to energy differences compatible with CCSD(T) ones. Having in mind that CCSD(T) transition energies are likely to be of a good quality here, it seems reasonable to think that some cancelation of errors also exists for fixed-node DMC calculations based on Hartree-Fock nodes.

In order to have a complete description of the atomic transitions the relativistic contributions have to evaluated. In Table IV we present our numerical Dirac-Fock total energies for the various states studied and in Table V our final values obtained for transition energies when combining contributions from relativity and electronic correlation. According to our basic assumption [Eq. (2)] transition energies can be written as

$$\Delta E \simeq \Delta E^{\mathrm{rel}}(\mathrm{DF}) + \Delta E^{\mathrm{corr.nonrel}}, \tag{9}$$

where the relativistic contribution (Darwin, mass-velocity, and spin-orbit terms) is computed at the Dirac-Fock level and the electron correlation contribution at the nonrelativistic level. ΔE^{Rel} (DF) can be obtained by computing the differences of total energies presented in Table IV and $\Delta E^{\mathrm{corr.nonrel}}$ by computing the change in the correlation energies presented in Table II.

The results of Table V show that both CCSD(T) and DMC results (complemented with relativistic contributions) are in excellent agreement with the experimental data. Let us emphasize that relativistic effects are not negligible. Indeed, at the nonrelativistic level (see Table III) the $^2S \rightarrow {}^2D$ transition energy is about 3000 cm^{-1} greater than the experimental J-averaged value (12 019 cm^{-1}), the $^2S \rightarrow {}^2P$ value is about 1000 cm^{-1} too small (expt.: 30 618 cm^{-1}), and the first ionization potential (IP) is also found to be too small by an amount close to 1600 cm^{-1} (expt.: 62 317 cm^{-1}).

When including the relativistic effects the errors on the CCSD(T) results vary between 80 and 440 cm^{-1}. Note that the FN-DMC error bars (about 1600 cm^{-1}) are large enough to include both CCSD(T) and experimental values. We remark that our CCSD(T) value of 61 875 cm^{-1} for the IP can be compared with a previously obtained CCSD fully numerical result[41] of 60 967 cm^{-1}; this allows us to estimate the contribution of the triple excitations to be around 1000 cm^{-1} on the IP.

Let us emphasize that the spin-orbit splittings of both atomic transitions ($^2S \rightarrow {}^2D$ and $^2S \rightarrow {}^2P$) are quite well reproduced at the Dirac-Fock level. This result, which shows that there is a rather weak coupling between the spin-orbit and correlation effects, supports our initial hypothesis concerning the effective decoupling between relativity and correlation. Finally, in spite of the not so large Z value for Copper (Z=29) it is crucial to recognize that relativistic effects play an essential role in the spectroscopy of this atom. To illustrate this important point we present in Figs. 1 and 2 a pictorial representation of the respective roles of relativity and nonrelativistic correlation in the construction of the energy of each component Cu $^2S \rightarrow {}^2D_{J=5/2,3/2}$, and ^2S

TABLE V. Final transition energies between the low-lying states of copper including relativistic effects computed at the Dirac-Fock level and nonrelativistic correlation energies with FN-DMC and CCSD(T). Experimental results are taken from Ref. 40. Energies in wave numbers. Statistical errors on the last digit in parentheses for DMC data.

	J	$\Delta E^{\mathrm{rel}}_{\mathrm{DF}}$	$\Delta E^{\mathrm{rel}}_{\mathrm{DF}}+\Delta E^{\mathrm{corr.nonrel}}_{\mathrm{CCSD(T)}}$	$\Delta E^{\mathrm{rel}}_{\mathrm{DF}}+\Delta E^{\mathrm{corr.nonrel}}_{\mathrm{FN\text{-}DMC}}$	Expt.
Cu $^2S \rightarrow {}^2D$	5/2	−1738	11 123	10 333(1 405)	11 203
	3/2	770	13 631	12 841(1 405)	13 245
Cu $^2S \rightarrow {}^2P$	1/2	25 635	30 529	31 122(1 552)	30 535
	3/2	25 817	30 711	31 304(1 552)	30 784
Cu $^2S \rightarrow \mathrm{Cu}^+ \ {}^1S$ (IP)	0	52 964	61 875	61 304(1 714)	62 317

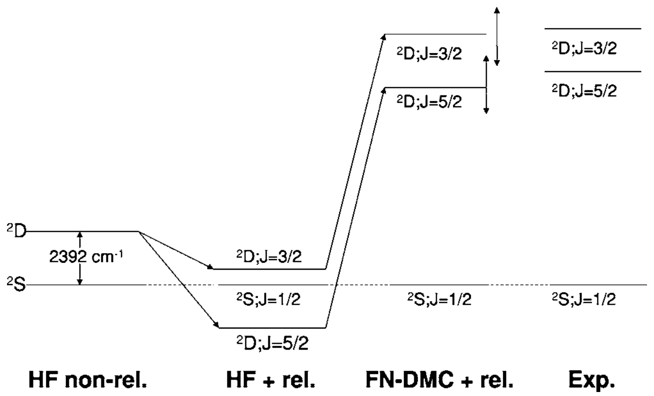

FIG. 1. Pictorial representation of the $^2S \rightarrow {}^2D$ transition with the various contributions considered. The SCF transition energy of 2392 cm^{-1} is indicated to set the scale. The vertical arrows in the FN-DMC+rel. column denote the statistical errors.

$\rightarrow {}^2P_{J=3/2,1/2}$, respectively. Clearly, relativity plays a central role in the spectroscopy of even such a light atom. In particular, note that relativity puts the lowest component of the D doublet below the relativistic ^2S ground state and that correlation effects are needed to recover the correct energetic differences between these states.

IV. CONCLUSIONS

In this work we have presented a complete analysis of the role of the relativity and electronic correlation in the transition energies between the low-lying states of the copper atom and its cation. Our final values for the transition energies are found to be in excellent agreement with experimental data. The relativistic calculations have been performed at the Dirac-Fock level using a basis-set-free description while the correlation effects have been treated either through all-electron CCSD(T) or fixed-node diffusion Monte Carlo. The usual assumption concerning the decoupling between relativity and electronic correlation for a light atom such as copper has been made and verified.

The primary goal of this work was to assess whether or not *all-electron* fixed-node diffusion Monte Carlo techniques could be successfully applied to the accurate calculation of the low-lying electronic states of high-Z systems involving highly-correlated $3d$ electrons. Several QMC calculations on metal-containing systems have been published but they all make use of effective core potentials to represent the effects of the innermost electrons. To the best of our knowledge we present here the first accurate all-electron FN-DMC calculations for a transition-metal system. The accuracy achieved in this work is about 0.15 eV, an error comparable to that obtained in pseudpotential-based DMC calculations. However, the nature of the errors in both approaches are quite different. In our all-electron calculations the final error is essentially of statistical nature and, therefore, can be reduced by increasing the length of the simulations. Here, the calculations have been quite extensive since each of the four electronic states has required about 2000-h CPU on a single Power4 processor. However, such calculations are presently accessible using parallel computations on machines having a moderate number of processors. The fact that QMC approaches parallelize trivially is clearly a major advantage with respect to more standard *ab initio* correlated methods. Besides the statistical error, there is one more error left, the fixed-node error. In contrast with the statistical error, it is a systematic bias and there is no simple way of decreasing it just by performing longer computations. In this work, we have found that the fixed-node error on the differences of energies of the low-lying states of the copper is smaller than the 0.15 eV statistical error when Hartree-Fock nodes are employed. Such a result is of course very encouraging for the use of the all-electron approach for more complex metal-containing systems. However, it should be noted that in recent FN-DMC studies using ECPs,[25,26] some influence of the choice of the nodal hypersurfaces (resulting either from Hartree-Fock or Kohn-Sham orbitals) has been observed in the binding energy of MnO and TiO (Ref. 25) and in the dissociation energy of transition-metal carbonyls.[26] Now, regarding DMC calculations with pseudopotentials two additional systematic errors show up: the pseudopotential itself and the localization error. The error due to the pseudopotential can be easily evaluated by making comparaisons between results obtained from traditional high-quality *ab initio* calculations with and without pseudopotentials. For the $3d$ transition metal this error is estimated to be at most 0.1 eV.[20] The magnitude of the localization error is much more difficult to evaluate since it is intimately mixed with the fixed-node error. In the work presented by Flad and Dolg,[20] this error is found to vary between 0.1 and 0.5 eV depending on the type of trial wave functions used, the occupation of the $3d$ and $4s$ shells, and on the quantity evaluated. In this work we have shown that it is possible to avoid these two latter sources of systematic error by making all-electron FN-DMC calculations. This is clearly an advantage when one is interested in accurate estimation of the total nonrelativistic correlation energies of transition-metal-containing systems. For instance in the $CuCl_2$ case studied by two of us[42–44] this nonrelativistic correlation energy, which determines whether the ground state is of $^2\Sigma_g^+$ or $^2\Pi_g$ nature, has been particularly difficult to obtain accurately by highly correlated *ab initio* methods, even with the most sophisticated multireference CI approaches. The accuracy needed to distinguish between the two states has to be smaller than 0.04 eV, a precision which appears difficult to attain with ECP-FN-DMC calculations (all-electron QMC calculations for this problem are in progress[45]). On the other hand, to be fair it should be mentioned that the ECP approach presents an important practical advantage with re-

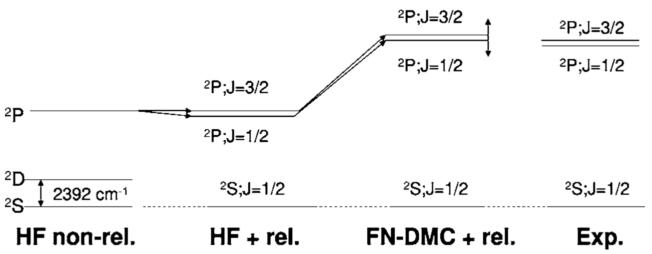

FIG. 2. Pictorial representation of the $^2S \rightarrow {}^2P$ transition with the various contributions considered. The SCF transition energy of 2392 cm^{-1} between the ^2S and ^2D states is indicated to set the scale. The vertical arrows in the FN-DMC+rel. column denote the statistical errors.

spect to all-electron calculations since it allows to include, in a very convenient way, the scalar relativistic effects, which for larger Z atoms are absolutely crucial.[46]

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