Quantum Monte Carlo for 3d Transition-Metal Atoms[†]

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The domain Green's function Monte Carlo method has been used to calculate the ground-state energy of the atoms Sc through Zn. The fixed node approximation with single-configuration explicitly correlated wave functions is used. A comparison with variational Monte Carlo energies is carried out. The quality of the ground-state energies reported here is similar to that achieved for few-electron atoms using similar techniques.

1. Introduction

Quantum Monte Carlo (QMC) methods provide the ground-state energy of a quantum system by using random walks. Nowadays, QMC methods are considered as powerful techniques that are used in a wide range of many-body problems, obtaining accurate results.[1] Seminal applications of QMC to the electronic structure of atomic and molecular systems were based on the formal analogue between the time-dependent Schrödinger equation and the diffusion equation and were restricted to few-electron systems.[2−4] Contrary to other many-fermion systems, such as, for example, liquid ^{3}He for which simulations with more than 100 particles have been carried out, only atoms with a few number of electrons have been systematically studied by using QMC techniques; see, for example, refs 5−12. Applications to heavier atoms in all-electron calculations are much more scarce.[13−16] Some atomic species, such as, for example, transition-metal atoms, present a very complex electronic structure with many electrons located in small regions and a strongly inhomogeneous charge distribution induced by the shell structure of the electronic density. These facts along with the large fluctuations induced by the core electrons have hindered the application of QMC to these atoms.

Our purpose in this work is to use QMC methods to systematically study medium size atoms in an all-electron calculation. In particular, we tackle here the calculation of the ground-state energy of the 3d transition-metal atoms, that is, from Sc to Zn. We use the domain Green's function Monte Carlo (GFMC)[17] with the fixed node approximation; see, for example, ref 18. The structure of this work is as follows: in section 2, we discuss the methodology, giving some details of the guiding function; in section 3, we show the results here obtained. Finally, Conclusion and Perspectives of this work can be found in section 4. Atomic units are used throughout this work.

2. Methodology and Wave Function

In QMC methods, the system is represented as a set of coordinates usually called walkers. An iterative procedure is applied to these walkers, making the set of configurations evolve in the configuration space of the system. Convergence is achieved when the distribution of the walkers is governed by the ground-state wave function. Formally, we start from the following integral equation[17]

$$\Psi^{(m)}(R) = (E_t + E_c) \int dR' G(R, R') \Psi^{(m-1)}(R') \qquad (1)$$

where R stands for the set of coordinates of the particles, E_t is taken approximately equal to the ground-state energy, E_c is a positive constant chosen such that the spectrum is positive, and $G(R, R')$ is the time-independent Green's function

$$(H + E_c)G(R, R') = \delta(R, R')$$

In the limit of large m, $\Psi^{(m)}$ converges to the lowest-energy eigenvector of the Hamiltonian. In practice, the value of the constant E_c does not affect the result; it is only relevant for the rate of convergence of the solution. In this work, we have used a value of E_c that is about 3% larger than the absolute value of the ground-state energy.

The Green's function is not known analytically for the N-electron Hamiltonian. In the domain GFMC method, the Green's function is expanded in an infinite series in terms of a known N-particle Green's function. In this series, the exact Green's function is obtained recursively. The series is summed exactly by using Monte Carlo, that is, by sampling each term of the series with a probability proportional to its weight. Once one term is selected, its contribution to the integral given in eq 1 is simulated by using random walks. This leads to the fact that a GFMC step consists of an intermediate walk. Depending on the element of the series sampled, the new walker generated may not be part of the new generation and must be iterated again. Once all of the intermediate walkers and all their offspring have been processed and no new intermediate walkers have been created, one continues to the next generation.[1] The size of the intermediate walk depends on the E_c value;[19] a large value of this constant reduces the number of intermediate walkers, in such a way that in the limit of infinite E_c, one obtains the short-time-step approximation with only one step, that is, diffusion Monte Carlo. The larger the E_c value, the larger the number of GFMC steps that must be taken in order to achieve convergence;

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if one reduces E_c, each step is more involved, but a lower number of them is required to sample the configuration space. With the E_c values used here, the number of internal steps for the system studied here varies between 500 and 600. For a detailed discussion of the method, see, for example, refs 17−19.

The procedure is exact for bosons and is effected only by the statistical error. For fermions, the fixed node approximation[3,4] is applied. This is a modification of the method that provides an upper bound to the exact ground-state energy. It is based in an approximate knowledge of the nodes of the exact wave function that are included as an additional boundary condition to the Green's function.[18] If the exact nodes were used, one would obtain the exact energy.

Finally, a key point in practical implementation of the QMC methods in quantum chemistry problems is the use of the importance sampling technique. This is a variance reduction method that becomes very important in order to reduce the statistical fluctuations of the simulations and to obtain accurate, in the sense of low numerical uncertainty, results. The idea is to use an approximate wave function $\Psi_t(R)$ to guide the walk toward those regions where the system has a high probability. The more accurate the trial function, the larger the reduction of the statistical noise for a given simulation size. More details can be found in refs 1 and 19.

The trial wave functions for the atomic systems studied here are the explicitly correlated wave functions of ref 20. These functions are also used in the implementation of the fixed node approximation. The form of these trial functions is

$$\Psi_t(R) = F(R)\Phi(R) \tag{2}$$

where $F(R)$ is the correlation factor and $\Phi(R)$ the model function. The correlation factor depends explicitly on the interelectronic coordinates and is written as[6]

$$F = \mathrm{e}^{\sum_{i<j} U_{ij}}$$

where

$$U_{ij} = \sum_{k=1}^{N_c} c_k (\bar{r}_i^{m_k} \bar{r}_j^{n_k} + \bar{r}_i^{n_k} \bar{r}_j^{m_k}) \bar{r}_{ij}^{o_k}$$

and

$$\bar{r}_i = \frac{br_i}{1 + br_i} \qquad \bar{r}_{ij} = \frac{dr_{ij}}{1 + dr_{ij}}$$

The parameters c_k are fixed variationally,[20] and b and d are taken to be equal to one. The model function is antisymmetric and yields the proper values of the angular momentum and parity quantum numbers of the state under description. In this work, we use a single-configuration model function, which, in general, is a linear combination of Slater determinants with orbitals fixed, by using the parametrized optimized effective potential method.[21]

3. Results

In Table 1, we report the GFMC results for the ground-state energy of the atoms Sc to Zn. The corresponding Hartree−Fock energy as well as the variational Monte Carlo (VMC) energy obtained from these trial wave functions is also shown. In parentheses, we show the statistical error in the calculation, whereas in square brackets, the percentage of correlation energy recovered in the present calculation is shown. To calculate this percentage of correlation energy, we have considered as "exact" values the nonrelativistic energy reported in ref 22. It is worth mentioning that the accuracy of the "exact" values reported in ref 22 is not really known. All of the calculations have been carried out with average populations of 500 walkers and random walks of 20 blocks with 200 steps per block, and the number of internal steps was typically 500.

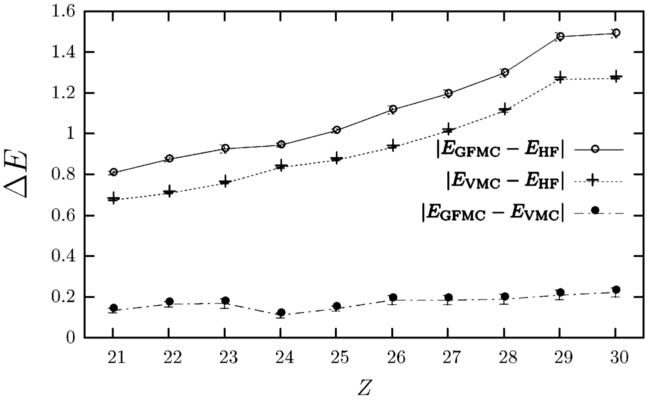

Figure 1. Correlation energy obtained in both GFMC and VMC calculations. The difference between those two calculations is plotted in the bottom part of the picture.

TABLE 1: HF, VMC, and GFMC Ground-State Energies for the Different Atoms Considered Here. In Parentheses, We Give the Statistical Error and in Square Brackets the Percentage of Correlation Energy Recovered. The Ground-State Configuration for the Different Atoms is [Ar]4s^{2}3d^n, except for Cr and Cu, Which are [Ar]4s3d^k, $k = 5$ and 10, Respectively

atom	E_{HF}[23]	E_{VMC}[20,24]	E_{GFMC}
Sc [^{2}D]	−759.73572	−760.411(2)[77]	−760.522(8)[90]
Ti [^{3}F]	−848.40600	−849.115(3)[77]	−849.28(1)[95]
V [^{4}F]	−942.88434	−943.642(3)[78]	−943.81(2)[95]
Cr [^{7}S]	−1043.3564	−1044.190(3)[86]	−1044.30(1)[97]
Mn [^{6}S]	−1149.8663	−1150.737(3)[82]	−1150.88(1)[95]
Fe [^{5}D]	−1262.4437	−1263.376(2)[79]	−1263.56(2)[94]
Co [^{4}F]	−1381.4146	−1382.426(3)[77]	−1382.61(2)[91]
Ni [^{3}F]	−1506.8709	−1507.981(4)[77]	−1508.17(2)[90]
Cu [^{2}S]	−1638.9637	−1640.231(3)[79]	−1640.44(2)[92]
Zn [^{1}S]	−1777.8481	−1779.119(2)[73]	−1779.34(2)[86]

The absolute value of the correlation energy recovered in the present GFMC calculation is shown in Figure 1 where it is compared with the corresponding VMC result.[20] This value increases smoothly with the atomic number in any of the two calculations, with a difference between the VMC and QMC energies that is nearly constant for the atoms studied here.

The atoms in the first half of the 3d shell as well as the iron atom present a percentage of correlation appreciably greater than 90%. Then, it decreases as the atomic number increases up to values around 90% and then decreases to 86% for Zn. These values are similar to the GFMC results obtained for the first-row atoms starting from trial functions with the same structure; see, for example, refs 8, 9, 12, and 25. For Cr and Cu, we have obtained that the percentage of correlation energy recovered is appreciably higher than that of their neighbor atoms, especially for Cu. This can be due to the near-degeneracy effect for which a pair of electrons in the *n*s shell can be promoted to the *n*p shell. This is a nondynamic correlation effect that is not properly described by the correlation Jastrow factor. Near degeneracy does not appear for Cr and Cu, for which the ground-state electronic configuration is [Ar]4s3d^5 and [Ar]4s3d^{10}, respectively. For these atoms, one expects that the nodal surface of a single-configuration model wave function, as that used here, constitutes a better approximation to the exact one than that for the rest of the atoms where configuration mixing is more important. At the variational level and working with a explicitly correlated wave function, a significant lowering in the ground-state energy was observed when a two-configuration wave function accounting for the near degeneracy of the single-particle levels was employed.[24] A similar improvement can be expected in a QMC calculation due to the variational nature of the fixed node approximation.

Finally, let us mention that very few quantum Monte Carlo results for 3d transitions-metal atoms have been found. It is worth mentioning here that in ref 15, a value of $-1640.411(5)$ au was obtained for the ground state of the Cu atom. This value practically coincides with the corresponding GFMC one here reported.

4. Conclusions and Perspectives

A systematic study using the all-electron quantum Monte Carlo method of the correlation energy of the ground state of the 3d transition-metal atoms has been carried out. Most of the previous similar studies had been restricted to light atoms or are based on the use of a pseudopotential. The present calculation yields an accurate value of the correlation energy of these systems, effected only by the fixed node error. The quality of the results is similar for all of the atoms studied.

Future work includes the use of multideterminant wave functions to improve the quality of the nodes and the study of excited states and charged species. These calculations would provide excitation energies, ionization potentials, and electron affinities. In order to compare with the experimental value, it is necessary to include relativistic effects, at least perturbatively as, for example, in refs 15 and 16.

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