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Accurate nonrelativistic ground-state energies of 3d transition metal atoms

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We present accurate nonrelativistic ground-state energies of the transition metal atoms of the 3d series calculated with Fixed-Node Diffusion Monte Carlo (FN-DMC). Selected multi-determinantal expansions obtained with the CIPSI (Configuration Interaction using a Perturbative Selection made Iteratively) method and including the most prominent determinants of the full configuration interaction expansion are used as trial wavefunctions. Using a maximum of a few tens of thousands determinants, fixed-node errors on total DMC energies are found to be greatly reduced for some atoms with respect to those obtained with Hartree-Fock nodes. To the best of our knowledge, the FN-DMC/(CIPSI nodes) ground-state energies presented here are the lowest *variational* total energies reported so far. They differ from the recently recommended non-variational values of McCarthy and Thakkar [J. Chem. Phys. **136**, 054107 (2012)] only by a few percents of the correlation energy. Thanks to the variational property of FN-DMC total energies, our results provide exact lower bounds for the absolute value of all-electron correlation energies, $|E_c|$. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4903985>]

I. INTRODUCTION

An accurate knowledge of nonrelativistic ground-state energies of atoms is known to be of great interest for computational chemistry. Atomic total energies are indeed routinely used to calibrate theoretical studies in electronic structure theory. For example, let us cite the search for more accurate exchange-correlation energy functionals in Density Functional Theory (DFT), the calibration of various approximations in wavefunction-based approaches (finite basis set effects, truncation at a given order in multi-particle excitations, etc.), the study of the fixed-node approximation in quantum Monte Carlo (QMC), the definition of alternative/exotic electronic approaches, etc. Furthermore, by combining experimental results and accurate nonrelativistic values, some valuable information about relativistic effects can also be obtained.

Here, accurate nonrelativistic, clamped nucleus, all-electron ground-state energies for the metal atoms of the 3d series (from Sc to Zn) are reported. Calculations are performed using the Fixed-Node Diffusion Monte Carlo (FN-DMC) approach, a QMC method known to be particularly powerful for computing ground-state energies.^{1,2} An overwhelming number of works have been devoted to the calculation of accurate atomic ground-state energies using various highly correlated approaches; here, we shall only restrict ourselves to give the typical accuracies presently achievable. For small atoms (say, less than 10 electrons, that is, from H to Ne for neutral atoms), very accurate values with errors smaller than 10^{-4} – 10^{-5} a.u. (or much smaller for the lightest atoms) can be obtained. For heavier atoms up to Ar (18 electrons), the accuracy reduces to the millihartree level (\sim chemical accuracy). For even bigger atoms to obtain a precision close to the millihartree is problematic and only a small number of

results have been published. Regarding quantum Monte Carlo studies using FN-DMC or a closely related QMC variant, most of the works have been concerned with atoms from Li to Ne; for the most recent ones, see, e.g., Refs. 3–6. For heavier atoms, most calculations have been performed using pseudo-potentials to remove core electrons (see, e.g., Refs. 7–9). At the all-electron level, very little has been done. We can essentially cite the FN-DMC calculations by Ma *et al.*¹⁰ for the Ar, Kr, and Xe atoms; calculations for the Cu atom and its cation,^{11,12} and two studies by Buendia and collaborators for 3d transition metal atoms.^{4,6}

It is fair to say that FN-DMC is presently the most accurate method for computing total ground state energies for large enough electronic systems. Potentially, diffusion Monte Carlo allows an exact stochastic solution of the Schrödinger equation. Several sources of error make, in practice, FN-DMC simulations non-exact. However, most of the errors are not of a fundamental nature and can be easily kept under control (mainly, the statistical, finite time-step, and population control errors). In contrast, the fixed-node error resulting from the use of trial wavefunctions with approximate nodes is much more problematic since, up to now, no simple and systematic scheme to control this error has been devised. Note that the fixed-node approximation is variational, $E_{\text{FN}} \geq E_0$, a convenient property to get upper and lower bounds for total energies and absolute values of correlation energies, respectively [in contrast, e.g., with the non-variational character of the commonly used Coupled Cluster with Singles, Doubles and Triples perturbatively (CCSD(T)) or Møller-Plesset approaches].

To decrease the fixed-node error, the common strategy is to use high-quality trial wavefunctions and to resort to multi-parameter stochastic optimization techniques to get the best parameters (usually via minimization of the total energy and/or its variance). A great variety of functional forms

have thus been introduced for the wavefunction (see, e.g., Refs. 12–22), and various optimization techniques designed to be efficient in a Monte Carlo context have been developed (e.g., Ref. 23).

In this work, we shall employ a different strategy based on the use of a new class of trial wavefunctions very recently introduced in QMC simulations.²⁴ The key ideas are (i) to avoid the use of a Jastrow factor, (ii) to rely on standard multi-determinant configuration interaction (CI) expansions, and (iii) to avoid any stochastic optimization of the wavefunction. To build CI expansions compact enough to make QMC feasible in practice, we employ a selected CI method (CIPSI (Configuration Interaction using a Perturbative Selection made Iteratively) algorithm, see Refs. 26 and 32) allowing to extract the most prominent determinants of the Full Configuration Interaction (FCI) expansion. Using an efficient implementation of the calculation of the multi-determinant part^{34,35} expansions containing a large number of determinants can be used in QMC. In the present application to $3d$ atoms, expansions up to a few tens of thousands of determinants have been employed. A nice feature of using CIPSI wavefunctions is that simulations can be performed in a fully black-box way: The CI program is first run, then the QMC code is started using as input the CI wavefunction directly as it comes from the output of the CI program. In particular, the preliminary multi-parameter Monte Carlo optimization of the trial wavefunction done in standard FN-DMC approaches (see, e.g., Ref. 36) is avoided. A number of recent applications^{24,37,38} have illustrated that CIPSI trial wavefunctions are effective in improving nodes. Furthermore, the fixed-node energy is found to decrease monotonically as a function of the number of determinants or the size of the basis set. This remarkable property allows to define a simple control of the fixed-node error. The price to pay for such attractive properties is that Jastrow-free CI expansions have (much) larger variances and thus require longer simulation times. However, this aspect is in practice not as critical as it may appear. By using our efficient implementation of the calculation of the multi-determinant part and by running our QMC code on medium size computational platforms with a few thousands of compute cores, it has been possible to realize the entire set of calculations presented here for the $3d$ series in less than two days. From a more general perspective, we would like to emphasize that the possibility of having a simple, automatic, and systematic way of decreasing and controlling the fixed-node bias is of utmost practical importance. It clearly remains true even at the price of more central processing unit-intensive simulations that will anyway become more and more easy to perform in view of the embarrassingly parallel property of QMC and the rapid development of ever more powerful parallel machines.

The FN-DMC/(CIPSI nodes) total ground-state energies of metal atoms of the $3d$ series obtained here are compared to the very recent results of Buendia *et al.*⁶ using a FN-DMC-type approach with a single-determinant trial wavefunction. A systematic improvement in FN total energies is obtained for all atoms, except for Zn for which similar results are found. For the lightest $3d$ atoms, the total energy values are much improved (a gain up to about 4.5×10^{-2} a.u. for Sc).

To the best of our knowledge, the data presented here are the lowest variational total ground-state energies reported so far for the $3d$ transition metal atoms. They differ from the recently recommended non-variational values of McCarthy and Thakkar³⁹ (denoted as McCT in what follows) obtained by an hybrid approach combining MP2 results at complete-basis-set (CBS) limit and accurate CCSD(T) values, only by a few percents of the correlation energy, namely, between 5.6% and 8% while these authors estimate their errors to be about $\pm 3\%$. Thanks to the variational property of FN-DMC total energies, our results also provide exact lower bounds for the absolute value of all-electron correlation energies, $|E_c|$.

II. METHODS AND COMPUTATIONAL DETAILS

A. CIPSI

The CIPSI method, and similar approaches closely related, have been introduced and developed a long time ago by a number of authors (see Refs. 25–33). In a few words, the approach consists in building the multi-determinantal expansion *iteratively* by selecting at each step one determinant (or a group of determinants) according to a perturbative criterion. A determinant D_i (or a group of determinants) is added to the current wavefunction if its (their) energetic contribution(s) calculated by second-order perturbation theory is (are) sufficiently large. In this way, the wavefunction is built hierarchically, the most important determinants of the FCI solution entering first in the expansion. Such a construction must be contrasted with standard approaches (configuration interaction with singles, configuration interaction with singles and doubles, etc.), where the contributions at a given order are calculated by considering all possible particle-excitations with respect to some reference wavefunction (usually, the Hartree-Fock (HF) solution). The CIPSI multi-determinantal expansion is thus much more compact than standard expansions, an important practical point for FN-DMC where the trial wavefunction and its derivatives must be computed a very large number of times during the simulations. Let us now briefly summarize the algorithm. More details can be found in Ref. 24 and references therein.

In multi-determinantal expansions, the ground-state wavefunction $|\Psi_0\rangle$ is written as a linear combination of Slater determinants $\{|D_i\rangle\}$, each determinant corresponding to a given occupation by the N_α and N_β electrons of $N = N_\alpha + N_\beta$ electrons among a set of M spin-orbitals $\{\phi_1, \dots, \phi_M\}$ (restricted case). The best representation of the exact wavefunction in the entire determinantal basis is the FCI wavefunction written as

$$|\Psi_0\rangle = \sum_i c_i |D_i\rangle, \quad (1)$$

where c_i are the ground-state coefficients obtained by diagonalizing the Hamiltonian matrix, $H_{ij} = \langle D_i | H | D_j \rangle$, within the orthonormalized set, $\langle D_i | D_j \rangle = \delta_{ij}$, of determinants $|D_i\rangle$.

In its simplest form, the multi-determinant wavefunction is iteratively built as follows. Let us call $|\Psi_0^{(n)}\rangle = \sum_{i \in S_n} c_i^{(n)} |D_i\rangle$ the current wavefunction at iteration n , where S_n is the set

of selected determinants at iteration n . Typically, at the initial step $n = 0$, a mono-determinantal HF-type or a short complete-active-space-self-consistent-field-type wavefunction is used. The first step consists in collecting all *different* determinants $|D_{ic}\rangle$ connected by H to $|\Psi_0^{(n)}\rangle$, that is, $\langle\Psi_0^{(n)}|H|D_{ic}\rangle \neq 0$. Then, the second-order correction to the total energy resulting from each connected determinant is computed,

$$\delta e(|D_{ic}\rangle) = -\frac{\langle\Psi_0^{(n)}|H|D_{ic}\rangle^2}{\langle D_{ic}|H|D_{ic}\rangle - E_0^{(n)}} \quad (2)$$

and the determinant (or group of determinants) $|D_{ic}^*\rangle$ associated with the largest $|\delta e|$ (or greater than a given threshold) is (are) added to the reference subspace

$$S_n \rightarrow S_{n+1} = S_n \cup \{|D_{ic}^*\rangle\}.$$

Finally, the Hamiltonian matrix is then diagonalized within S_{n+1} to obtain the new wavefunction at iteration $n + 1$ and the process is iterated until a target size N_{dets} for the reference subspace is reached. The CIPSI wavefunction issued from this selection process is the trial wavefunction used here for FN-DMC.

B. FN-DMC

For a detailed presentation of the theoretical and practical aspects of FN-DMC, the reader is referred to the literature, e.g., Ref. 40. Here, let us just emphasize that the central quantity of such approaches is the trial wavefunction Ψ_T determining both the magnitude of the fixed-node error through its approximate nodes and the quality of the statistical convergence (good trial wavefunctions imply small statistical fluctuations). The computational cost of FN-DMC is almost entirely determined by the evaluation at each Monte Carlo step of the value of Ψ_T and its first (drift vector) and second derivatives (Laplacian needed for the local energy). In view of the very large number of MC steps usually required (typically at least billions and often much more), it is essential to compute such quantities very rapidly. In the present work, the typical size of the expansion considered is a few tens of thousands of determinants. Some care is thus required when computing such expansions to keep the computational cost reasonable. The various aspects regarding this problem are presented in Ref. 35.

C. Computational details

The atomic basis sets used for the calculations are the Slater-type orbitals of Bunge⁴¹ supplemented with four additional $4f$ and three $5g$ functions (a total of 112 atomic basis functions). All the CIPSI calculations have been performed using Hartree-Fock molecular orbitals using the code developed in our group (quantum package), and all the FN-DMC calculations have been performed using QMC = Chem.⁴²

For each atom, the CIPSI calculation was stopped when more than 10^6 determinants were selected in the variational wave function. This wave function was then truncated such that the least significant determinants contributing to 0.5% of

the norm of the wave function were discarded: 10^4 – 5×10^4 determinants were kept. This wave function was used *without any modification* as the trial wave function for the FN-DMC calculations (no Jastrow factor).

For the FN-DMC calculations, we have employed the algorithm described in Ref. 43 allowing us to use a small constant number of walkers. A block consisted of 30 walkers performing 5000 steps with a time step of 10^{-5} a.u., a value chosen such that the time-step error was smaller than the statistical error. Long enough simulations have been performed to make the statistical error negligible with respect to the fixed-node one: depending on the atom, a number of blocks between 7×10^4 and 1.5×10^5 were calculated ($\sim 10^{10}$ MC steps).

III. RESULTS

In Table I, the variational energy, the number of determinants in the CIPSI expansion, an estimate of the percentage of the total CE recovered, and the average value of the S^2 total spin operator for each trial wavefunction Ψ_T used in FN-DMC are given. The CE's reported are calculated from the recommended values of McCarthy and Thakkar.³⁹ We emphasize that, in contrast with the present work, these values have not been computed directly from a unique (very) accurate energy calculation but have been obtained indirectly by combining Møller-Plesset (MP2) correlation energies extrapolated at the CBS limit and CCSD(T) calculations using Dunning's basis sets of various sizes. The percentages of correlation energies retrieved at the CIPSI variational level are found to be around 60%. It is important to note that the correlation effects recovered in such CI calculations are mostly *valence* correlation effects (valence basis set) and *non-dynamical* correlation effects resulting from the use of multi-determinant expansions including the most prominent determinants. In particular, most of the energetic core contributions are not taken into account in these valence CI calculations. Some caution is thus needed when comparing the total energies obtained with the Slater-Jastrow wavefunctions usually employed in FN-DMC and the valence CI wavefunctions proposed here. Finally, note that the total

TABLE I. Number of determinants, N_{dets} , of the CIPSI expansion used as FN-DMC trial wavefunction. Variational energy, E_{var} (CIPSI), estimated percentages of the correlation energy (CE) recovered, and eigenvalue of the S^2 spin operator. Energy in hartree.

Atom	N_{dets}	E_{var} (CIPSI)	(CE in %)	S^2
Sc $^2D(d^1s^2)$	11 389	−760.32556	(66.5)	0.75
Ti $^3F(d^2s^2)$	14 054	−849.02624	(66.9)	1.99
V $^4F(d^3s^2)$	12 441	−943.53667	(64.9)	3.74
Cr $^7S(d^5s^1)$	10 630	−1044.03692	(63.6)	11.97
Mn $^6S(d^5s^2)$	11 688	−1150.57902	(63.0)	8.73
Fe $^5D(d^6s^2)$	13 171	−1263.21805	(62.5)	5.99
Co $^4F(d^7s^2)$	15 949	−1382.24964	(62.8)	3.74
Ni $^3F(d^8s^2)$	15 710	−1507.74694	(62.3)	1.99
Cu $^2S(d^{10}s^1)$	48 347	−1639.96605	(63.3)	0.75
Zn $^1S(d^{10}s^2)$	44 206	−1778.82784	(60.5)	0.00

TABLE II. FN-DMC total energies for the $3d$ series of transition metal atoms together with the percentage of correlation energy recovered for different nodal structures. Energy in hartree.

Atom	HF nodes	(CE in %)	OEP nodes ^a	(CE in %)	CIPSI nodes	(CE in %)	FN energy gain with CIPSI nodes ^b
Sc	-760.5265(13)	[89.2(2)]	-760.5288(6)	[89.50(7)]	-760.5718(16)	[94.4(2)]	-0.0453(21)
Ti	-849.2405(14)	[89.6(2)]	-849.2492(7)	[90.55(7)]	-849.2841(19)	[94.2(2)]	-0.0436(24)
V	-943.7843(13)	[89.6(1)]	-943.7882(6)	[89.95(6)]	-943.8234(16)	[93.4(2)]	-0.0391(21)
Cr	-1044.3292(16)	[91.0(2)]	-1044.3289(6)	[90.93(6)]	-1044.3603(17)	[93.9(2)]	-0.0311(23)
Mn	-1150.8880(17)	[90.4(2)]	-1150.8897(7)	[90.54(6)]	-1150.9158(20)	[92.9(2)]	-0.0278(26)
Fe	-1263.5589(19)	[90.1(2)]	-1263.5607(6)	[90.26(5)]	-1263.5868(21)	[92.4(2)]	-0.0279(28)
Co	-1382.6177(21)	[90.5(2)]	-1382.6216(8)	[90.85(6)]	-1382.6377(24)	[92.1(2)]	-0.0200(32)
Ni	-1508.1645(23)	[91.6(2)]	-1508.1743(7)	[92.27(5)]	-1508.1901(25)	[93.4(2)]	-0.0256(34)
Cu	-1640.4271(26)	[92.4(2)]	-1640.4266(7)	[92.34(4)]	-1640.4328(29)	[92.7(2)]	-0.0057(39)
Zn	-1779.3371(26)	[91.9(2)]	-1779.3425(8)	[92.24(5)]	-1779.3386(31)	[92.0(2)]	-0.0015(40)

^aReference 6.^bDifference between FN-DMC energies obtained with HF nodes (column 1) and newly proposed CIPSI nodes (column 5).

spin values S^2 obtained from the truncated CIPSI expansions show that the trial wavefunctions built are almost pure spin-eigenstates.

In Table II, the fixed-node DMC total energies obtained using standard Hartree-Fock nodes and newly proposed CIPSI nodes are reported. For the sake of comparison, we also give the very recent results of Buendia *et al.*⁶ that were up to now the lowest variational fixed-node energies reported for these atoms. In their study, the trial wavefunctions employed are written as the product of a nodeless correlation factor and a so-called model function obtained within the parametrized Optimized Effective Potential (OEP) approximation. The model function determining the nodal structure is written as a linear combination of a few Configuration State Functions (CSFs), mainly to take into account $4s$ - $4p$ near-degeneracy effects. For the Cr and Cu atoms with a singly occupied $4s$ shell, the model function is represented by a single CSF, while for the other atoms $4s^2 3d^n$ and $4p^2 3d^n$ configurations are mixed. For each type of nodes used, an estimate of the percentage of the correlation energy is also reported. The percentages retrieved by all FN-DMC calculations presented are important and range between 89% and 94%. A first observation is that energies resulting from HF and OEP nodes are of comparable quality, while CIPSI nodes may lead to significantly lower fixed-node energies. The gain in energy with the new nodes is found to decrease almost uniformly with Z . For the lightest elements (Sc, V, and Ti), a maximum gain of about 0.045 a.u. is achieved; for the intermediate atoms (Cr–Ni), about 0.02–0.03 a.u. is obtained, while for the two heaviest elements (Cu and Zn), no gain is observed within statistical fluctuations. The fact that CIPSI performs better for lightest elements is not surprising since Hartree-Fock nodes are known to be well-adapted to atoms with spherical symmetry. In the extreme case of the Cu and Zn atoms having a totally filled and spherically symmetric $3d$ shell, HF and CIPSI nodes give similar results. In the opposite case of light atoms, the CIPSI wavefunctions, that have many more degrees of freedom than the single-configuration HF solution to describe non-symmetrical electronic configurations, lead to much improved results. In Table III, the correlation energies resulting from our FN-DMC simulations are reported and

compared to the recommended values of McCT. As already noted, these latter results have been obtained with a mixed approach including MP2-CBS and CCSD(T) calculations. According to the authors, the errors in these values are estimated to be $\pm 3\%$. The relative differences between FN-DMC/[HF nodes] or FN-DMC/[OEP nodes] and the McCT values go from 8% to 11%. Using CIPSI nodes, the differences are reduced and range between 6% and 8%. Note that the typical statistical error on these percentages is small and about 0.2%. Although our final values for correlation energies are slightly less accurate than the estimates made by McCT, we would like to emphasize and conclude on three important points: (i) In contrast with what has been done by McCT, our correlation energies have been directly computed with a unique highly correlated electronic structure method. No hybrid scheme mixing results of two different approaches has been employed. To the best of our knowledge, the FN-DMC values presented here are the most accurate (lowest) nonrelativistic total energies ever reported for the $3d$ transition metal atoms. (ii) As a consequence of the variational property of FN-DMC total energies and also in contrast with McCT's results, the absolute values of our correlation energies are *exact lower bounds* of the unknown CE's. (iii) Finally, in view

TABLE III. Fixed-node DMC correlation energies, $-E_c$, in hartree using HF and CIPSI nodes. Comparison with the recommended values of McCarthy and Thakkar (McCT).³⁹

Atom	HF nodes	OEP nodes ^a	CIPSI nodes	McCT ^b
Sc	0.7900(13)	0.7923(6)	0.8353(16)	0.8853
Ti	0.8454(14)	0.8541(7)	0.8890(19)	0.9433
V	0.9000(13)	0.9039(6)	0.9390(16)	1.0049
Cr	0.9728(16)	0.9725(6)	1.0039(17)	1.0695
Mn	1.0218(17)	1.0235(7)	1.0495(20)	1.1304
Fe	1.1122(19)	1.1140(6)	1.1401(21)	1.2343
Co	1.2016(21)	1.2055(8)	1.2216(24)	1.3270
Ni	1.3043(23)	1.3141(7)	1.3299(25)	1.4242
Cu	1.4634(26)	1.4629(7)	1.4691(29)	1.5842
Zn	1.4890(26)	1.4944(8)	1.4905(31)	1.6202

^aReference 6.^bReference 39.

of the great versatility of FN-DMC/CIPSI, there is no reason why improved lower bounds would not be achieved in the near future.

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