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Quantum Monte Carlo calculation of the Fe atom

Luboš Mitáš*
National Center for Supercomputing Applications, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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Variational and fixed-node diffusion Monte Carlo calculations for several states of the iron atom are presented. The Ne-core electrons are eliminated by accurate scalar relativistic pseudopotentials. Variational valence correlation energies are the largest obtained so far by any variational method including the most extensive quantum chemistry calculations. The average difference between experiment and diffusion Monte Carlo results for the $s \rightarrow d$ excitation energies, the ionization potential, and the electron affinity is 0.15 eV.

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Accurate electronic structure calculations of the late 3*d* transition-metal atoms such as Mn, Fe, Co, or Ni are among the long-standing problems in atomic physics. There are several factors which complicate the calculations [1–5]: (i) compactness and double occupancy of the *d* shell, (ii) the semicore character of 3*s* and 3*p* shells (they must be treated as valence shells in accurate calculations), (iii) the impact of relativistic effects on energy differences, and (iv) the near degeneracy of 3*d*, 4*s*, and 4*p* levels. The first two points are particularly significant and imply unusually large correlation energies, typically ≈ 20 eV or more.

The largest part of the 3*s*, 3*p*, and 3*d* correlation energy comes from a repulsive nonanalytic cusp in the wave function whenever two electrons come close together. This feature is difficult to describe within current correlated approaches in quantum chemistry and is responsible for a slow convergence of these methods [6]. This contrasts with the quantum Monte Carlo (QMC) approach which enables us to include the exact electron-electron cusp into the trial (variational) function in a straightforward and explicit way [7,8]. From this point of view the transition elements are ideal systems to demonstrate complementarity and competitiveness of QMC with the more standard quantum chemistry methods like coupled cluster or configuration interaction [9]. There has been remarkable progress in QMC recently [10,11] and one of the important achievements was the development of techniques for dealing with core electrons which previously hampered calculations beyond the first row because of the enormous core energy fluctuations [12–14]. Also, more general trial functions have significantly increased the accuracy and efficiency of calculations [6,15]. For the $H + H_2 \rightarrow H_2 + H$ reaction barrier, an accuracy record of 0.0004 eV has been established very recently [16]. Finally, a wide range of applicability of QMC methods has been demonstrated by successful solid-state calculations with more than 200 valence electrons [17,18].

So far there have been very few attempts to apply QMC to transition metals. We can mention the calculations of Sc and Y atomic ionization potentials [19] and QMC evaluation of CuH molecular properties [20]. We have carried out calculations of several third-row transition elements (Sc, Ti, Mn, Fe, and Cu) [21] using less accurate Ar-core pseudopotentials (so that 3*s* and 3*p* electrons were omitted from the valence space). In general, the obtained results were excellent with the exception of Mn and Fe excited states for which ≈ 0.5 eV discrepancies with experiment have been found. In this paper we present a systematic calculation of the iron atom in several states using accurate Ne-core pseudopotentials for elimination of core electrons. Our variational Monte Carlo (VMC) results give the largest amount of the valence correlation energy obtained in a variational type of calculation. The diffusion Monte Carlo (DMC) estimations of the first ionization potential, the electron affinity, and the $s \rightarrow d$ excitation energies agree with experiment within 0.2 eV, which is the highest overall accuracy achieved so far by any method.

Both variational and diffusion Monte Carlo have been described in several excellent review articles [7,10,11]; thus, we will give only a brief description of these methods. For a given Hamiltonian H and an optimized trial function $\Psi(R)$, the VMC energy is given by

$$E_{\mathrm{VMC}} = \frac{\int |\Psi(R)|^2 [H\Psi/\Psi] dR}{\int |\Psi(R)|^2 dR} , \tag{1}$$

where R denotes coordinates of electrons. The many-body integral (1) is evaluated by Monte Carlo sampling of the distribution

$$|\Psi(R)|^2 / \int |\Psi(R)|^2 dR$$

by the Metropolis algorithm.

The DMC technique is based on a stochastic simulation of the imaginary-time Schrödinger equation. Using the importance sampling by $\Psi(R)$, the Schrödinger equation can be arranged to the form

$$f(R, t+\tau) = \int G(R, R', \tau) f(R', t) dR' , \tag{2}$$

where

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*Permanent address: Institute of Physics, Dubravska cesta 9, 84228 Bratislava, Slovakia.

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$$f(R,t)=\Psi(R)\Phi(R,t)\ , \tag{3}$$

$$G(R,R',\tau)=\frac{\Psi(R)}{\Psi(R')}\langle R|\exp(-\tau H)|R'\rangle\ . \tag{4}$$

An accurate analytical expression for the propagator $G(R,R',\tau)$ can be written down for a sufficiently small τ [8,11]. The lowest energy solution with boundary conditions prescribed by fermionic nodes or other symmetry conditions is found by iteration of Eq. (2) to the large-t limit. In the case of a fixed-node approximation for fermions, which was used in this study, nodes of the solution $\Phi(R,t)$ are kept identical with the nodes of the trial function $\Psi(R)$.

To make the calculations feasible [13,14] for heavier atoms, we have used the *ab initio* pseudopotentials for eliminating the core electrons [22]. Hence, the valence Hamiltonian has the form

$$H_v=-\tfrac{1}{2}\sum_i \nabla_i^2+\sum_{i<j}\frac{1}{r_{ij}}+\sum_i v_{\mathrm{loc}}(r_i)+\sum_{i,l} v_l(r_i)\sum_m P_{lm}^{(i)}\ . \tag{5}$$

The last two terms represent the local and nonlocal parts of the pseudopotential and $P_{lm}^{(i)}$ denotes the ith electron projection operator on the spherical harmonic Y_{lm} (r_i denotes the distance of the electron from the nucleus; r_{ij} is the distance between two electrons).

For this study we have chosen the Ne-core (scalar relativistic) pseudopotentials constructed within the multiconfigurational Hartree-Fock approach with inclusion of relativistic effects [23] on the Cowan-Griffin level. The pseudopotentials were tested in the limited configuration interaction and for several states close to the ground state the all-electron energy differences were reproduced within ≈0.1 eV [23].

The diffusion Monte Carlo relies on the positivity of the Green's function involved in (4) and is problematic to use with the nonlocal operators. The reason is that the Green's function $\langle R|\exp(-\tau H_v)|R'\rangle$ with nonlocal H_v is not guaranteed to be positive definite for arbitrary R, R', and τ. However, as has been proposed previously, the nonlocal term can be evaluated with the trial function [13,14]. In effect, the last term in (5) is replaced by a many-body effective potential of the form

$$\left[\sum_{i,l} v_l(r_i)\sum_m P_{lm}^{(i)}\Psi\right]\Big/\Psi\ .$$

Because the modified Hamiltonian is not identical to (5), it is perhaps more appropriate to interpret the DMC energy as a perturbational correction to the variational estimation. This interpretation is supported by the fact that if $\Psi(R)$ approaches to exact eigenstate, then the DMC energy converges quadratically to the exact eigenvalue of the original Hamiltonian (5), as we have shown elsewhere [14]. In practice, we have found that it is possible to exploit this convergence and construct sufficiently accurate trial functions, producing excellent energy estimations. We will later discuss an additional test which was carried out in order to check the errors from nonlocal terms in DMC.

The trial function has a form similar to those used in other studies [6,15]:

$$\Psi(R)=\Psi_D(R)\exp\left[\sum_{i<j} u(r_i,r_j,r_{ij})\right]\ , \tag{6}$$

where $\Psi_D(R)$ is, in general, a linear combination of Slater determinant products (for spin-up and -down electrons):

$$\Psi_D(R)=\sum_n e_n D_n^{\uparrow} D_n^{\downarrow}\ , \tag{7}$$

while $u(r_i,r_j,r_{ij})$ includes two-body (electron-nucleus, electron-electron), and three-body (electron-electron-nucleus) terms and is described in detail elsewhere [21]. This correlation part is parametrized by 21 variational parameters which are optimized within VMC by minimizing the fluctuations of energy around its variational value [6,14,15,21]. The orbitals for Slater determinants were obtained by the numerical Hartree-Fock method and were represented by cubic splines in actual simulations. The trial function also included the excitation $4s^2 \rightarrow 4p^2$ for the cases when $4s$ orbital was doubly occupied in order to take into account the near-degeneracy effects [5].

The results for the total energies are summarized in Table I. In its lower part there is a comparison of correlation energies found by QMC and by the most extensive configuration-interaction and coupled-cluster calcula-

TABLE I. The valence total energies (a.u.) for the Fe atom in the restricted Hartree-Fock, variational, and diffusion Monte Carlo calculations using Ne-core pseudopotentials (statistical errors are in parentheses). Comparison of the valence correlation energy obtained by the coupled cluster [CCSD(T)] [3] with single, double, and perturbatively triple excitations, quadratic configuration interaction [QCISD(T)] [1], configuration interaction (CISD) [2], and present calculations is given in the lower part of the table.

Calculation	$^6D(3d^64s)$	$^3F(3d^8)$	$^5F(3d^74s)$	$^5D(3d^64s^2)$	$^4F(3d^74s^2)$
HF	−122.8812	−122.8226	−123.0388	−123.1144	−123.0278
VMC	−123.434(2)	−123.538(2)	−123.682(1)	−123.713(1)	−123.686(2)
DMC	−123.500(2)	−123.626(3)	−123.751(2)	−123.783(1)	−123.782(3)
CCSD(T)	0.478		0.563	0.534	0.603
QCISD(T)			0.564	0.528	
CISD			0.598	0.560	
VMC	0.554(2)	0.713(2)	0.644(1)	0.599(1)	0.650(2)
DMC	0.619(2)	0.803(3)	0.712(2)	0.668(1)	0.754(3)

TABLE II. VMC and DMC ionization potential (IP), electron affinity (EA), and excitation energies (eV) compared with experiment and with other calculations. CCSD(T) denotes coupled-cluster calculations of Urban, Bartlett, and Alexander [3]. QCISD(T) corresponds to quadratic configuration interaction of Raghavachari and Trucks [1], and CISD represents configuration interaction of Bauschlischer [2]. (Relativistic corrections were added to the results of nonrelativistic calculations from Refs. [1] and [3] so that they can be compared directly with experiment [25].)

Method	IP	${}^5D \rightarrow {}^3F$	${}^5D \rightarrow {}^5F$	EA
HF	6.35	7.94	2.06	−2.36
CCSD(T)	7.79		1.07	−0.16
QCISD(T)			1.07	
CISD			1.06	
VMC	7.61(6)	4.73(6)	0.84(4)	−0.72(6)
DMC	7.67(6)	4.24(9)	0.84(6)	−0.03(9)
Expt.	7.87	4.07	0.87	0.15

tions [1–3]. Although the valence correlation energies from the frozen-core approaches [1–3] and from our pseudopotential calculations are not exactly the same, one expects that they are very close because of the small size of the Ne core and also because of the small core-valence overlap. Thus, apart from small ambiguities because of the core treatment, it is evident that VMC calculations have already recovered more correlation energy than the quantum chemistry approaches. The largest part of the valence correlation energy ($\approx 85\%$) comes from the correlation factor with a relatively small number of variational parameters and a very compact form of the trial function. Obviously, the description of correlation effects by the optimized electron-electron cusp and "average backflow" [15] represented by three-body terms in (6) is very efficient when compared with slowly converging [2] configuration-interaction expansions for the wave function.

The energy differences, corresponding experimental values, and results of several other calculations are listed in Table II. In comparing our results with the previous calculations, one should keep in mind that a part of the differences can be caused by the different treatment of the core and relativistic effects [25]. The table shows that VMC gives the largest improvement, reducing significantly large Hartree-Fock errors. It is also interesting to observe that the variational bias is very small for the ionization potential and for ${}^5D \rightarrow {}^5F$ excitation energy, while it is significant for the other two energy differences. This implies lower accuracy of the trial function for the negative ion and ${}^3F$ state. The DMC corrects most of the remaining errors, achieving agreement with experiment within 0.2 eV, while the typical statistical error bar is 0.07 eV. Obviously, small systematic errors remain; the three most significant sources of them are the following: error already built in the pseudopotentials (≈ 0.1 eV) [23] which combines with a nonrigorous treatment of relativistic effects, error from evaluation of the nonlocal term, and the fixed-node error. In order to make the impact of the nonrigorous treatment of the nonlocal terms in the valence Hamiltonian (5) more transparent, we have carried out another set of DMC calculations where for the pseudopotential evaluation only $\Psi_D(R)$ was used instead of the $\Psi(R)$ (i.e., the last term in H_v was replaced by $[\sum_{i,l} v_l(r_i) \sum_m P_{lm}^{(i)} \Psi_D]/\Psi_D$). We have found that the total energies were higher but only by ≈ 0.1 eV, which we consider to be very small on the scale of total correlation energies. In addition, this small increase was very similar for all states so that the energy differences were unaffected within the error bars. This indicates that the impact of the nonlocal terms on the DMC simulations was small essentially because $3s$ and $3p$ electrons were in the valence space so that the radial range of pseudopotentials was rather restricted (less than 1 bohr). Thus we believe that the results represent excellent estimations of fixed-node energies of the valence Hamiltonian (5). Consequently, we consider our valence correlation energies to be the most accurate *ab initio* estimations to date. It is also interesting to estimate the all-electron correlation energy for the ground state (using an approximate value of 0.15 a.u. for the core-core and core-valence correlation from the all-electron calculations [3]). This gives 0.818 a.u. which compares favorably with the empirical value 0.831 a.u. of Szasz [24].

In conclusion, we have carried out high-accuracy quantum Monte Carlo calculations of the iron atom with Ne-core pseudopotentials. Using optimized trial functions, the diffusion Monte Carlo results reproduce the experimental affinity, the ionization potentials, and the excitation energies with the mean error 0.15 eV. The calculations demonstrate an increasing applicability and accuracy of quantum Monte Carlo calculations for systems with strong correlation effects and offer a promising alternative to traditional quantum chemistry methods.

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[25] The original nonrelativistic CCSD(T) values from Ref. [3] for the ionization potential, the $^5D \rightarrow {}^5F$ excitation energy, and the electron affinity are 7.73, 0.87, and 0.04 eV, respectively. However, the states with increasing d-shell occupancy exhibit increasing impact of relativistic effects which, unfortunately, makes the agreement with the experiment worse. Using the Cowan-Griffin approximate relativistic Hamiltonian [24] within the Hartree-Fock theory, one can estimate the relativistic corrections for the ionization potential and for the $^5D \rightarrow {}^5F$ excitation to be 0.06 and 0.22 eV [1,4], and for the electron affinity we have estimated this correction to be -0.20 eV. For the $^5D \rightarrow {}^5F$ excitation a similar value was found by Bauschlischer [2] by evaluating perturbatively the relativistic correction using the CISD wave function with a frozen Ne core.