

Accurate *Ab Initio* Calculation of Ionization Potentials of the First-Row Transition Metals with the Configuration-Interaction Quantum Monte Carlo Technique

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(Received 29 August 2014; revised manuscript received 10 November 2014; published 21 January 2015)

Accurate ionization potentials of the first-row transition-metal atoms are obtained via the initiator full configuration quantum Monte Carlo technique, performing a stochastic integration of the electronic Schrödinger equation in exponentially large Hilbert spaces, with a mean absolute error of 0.13 kcal/mol (5 meV). This accuracy requires correlation of the $3p$ semicore electrons and in some cases the $3s$ manifold, along with extrapolation of the correlation energies to the complete-basis-set limit, and provides a new theoretical benchmark for the ionization potentials of these systems.

DOI: 10.1103/PhysRevLett.114.033001

PACS numbers: 32.10.Hq, 31.15.V-

The chemical versatility of the $3d^n$ transition-metal atoms, which makes them key components in electron-transfer catalysis as well as numerous technological applications, derives in large part from their ability to exist in multiple oxidation as well as spin states [1–13]. Furthermore, electron removal energies are probed by spectroscopies such as photoemission and are also significant in theoretical terms, because the ionization potentials (IPs) determine the position of poles in spectral functions (such as frequency-dependent single-particle Green's functions) [14] and are therefore crucial references for Green's function theories of excitation energies [15,16]. The accurate theoretical treatment of IPs of these $3d$ systems has proven particularly challenging for *ab initio* theories. On the one hand, the removal of electrons leads to a significant rearrangement of the electronic configurations including changing the occupancy in the $3d$ shell, and, on the other, the concomitant shrinkage of the electron cloud results in a considerable contribution from dynamical correlation, the description of which requires large basis sets. In addition, scalar relativistic effects have been shown to play a significant role, typically contributing ~ 1.5 kcal/mol to the final result [17]. Recent work has estimated the size of this relativistic contribution by using the Douglas-Kroll-Hess theory [10,18–20] and has highlighted the importance of the interplay between correlation and relativistic effects. The relativistic multireference averaged coupled-pair functional theory with core-valence corrections yields a mean-absolute error (MAE) of 0.5 kcal/mol, while the most accurate calculations to date are based on a composite coupled-cluster approach taken to the single, double, triple, quadruple (CCSDTQ) level of theory [21] and improve the MAE to 0.3 kcal/mol.

In this Letter, we use the recently developed initiator full configuration-interaction quantum Monte Carlo (*i*-FCIQMC) technique to compute the IPs of the $3d$

transition-metal atoms. This technique is capable of converging upon an exact description of the correlated electronic wave functions expanded in extremely large Slater-determinant spaces while, through its annihilation step, suppressing the sign problem which plagues continuum space projector quantum Monte Carlo methods [22,23]. For example, in a recent study of the first-row dimers, spaces exceeding 10^{19} determinants were successfully sampled [24], rising to 10^{108} in a study of a 54-electron uniform electron gas [25]. Nevertheless, a number of significant challenges must be overcome, as a straightforward application of the *i*-FCIQMC method does not suffice. In the first place, it is necessary to work in the complete-basis-set limit, which can be approached only by basis-set extrapolation methods. This requires the correlation energies to be computed in basis sets of increasing cardinal number, which greatly impacts the computational cost. Second, as the systems considered consist of a relatively large number of electrons, it is prohibitive to perform all-electron calculations. While freezing electrons is simple within the *i*-FCIQMC method, the impact of so doing on the accuracy of the IPs must be determined. In particular, the $3s$ and $3p$ semicore electrons can significantly correlate with the valence electrons, but the correlation of all semicore electrons is computationally very expensive. Finally, to take account of scalar relativity, we use the Douglas-Kroll-Hess theory [26] with the associated augmented correlation-consistent polarized valence X -zeta (aug-cc-pVXZ-DK) basis sets [17,21] to compute the necessary one- and two-electron integrals [27].

We demonstrate that, with a judicious application of this methodology, it is indeed possible to improve substantially upon the accuracy reported in previous benchmark studies, yielding a new benchmark with a MAE of 0.13 kcal/mol. The study also highlights an intellectually pleasing feature of the *i*-FCIQMC method, in that the energies which it

TABLE I. Frozen-core i -FCIQMC ionization potentials in kcal/mol of the first-row transition metals. The number in parentheses denotes the error in the previous digit, $\sqrt{\delta E_{N-1}^2 + \delta E_N^2}$, with the values δE obtained through a Flyvbjerg-Petersen blocking analysis [34] of $E(\tau)$. The j -averaged experimental results E_{expt} [35–39] are also displayed, along with the term symbols and $4s3d$ occupancies of the neutral and cationic species.

System	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
X	$^2D(4s^23d^1)$	$^3F(4s^23d^2)$	$^4F(4s^23d^3)$	$^7S(4s^13d^5)$	$^6S(4s^23d^5)$	$^5D(4s^23d^6)$	$^4F(4s^23d^7)$	$^3F(4s^23d^8)$	$^2S(4s^13d^{10})$	$^1S(4s^23d^{10})$
X^+	$^3D(4s^13d^1)$	$^4F(4s^13d^2)$	$^5D(3d^4)$	$^6S(3d^5)$	$^7S(4s^13d^5)$	$^6D(4s^13d^6)$	$^3F(3d^8)$	$^2D(3d^9)$	$^1S(3d^{10})$	$^2S(4s^13d^{10})$
$E_{\text{ion}}^{(3)}$	147.797(1)	153.890(1)	157.258(4)	152.899(6)	169.387(5)	180.402(5)	186.144(3)	179.228(2)	176.282(4)	214.922(3)
$E_{\text{ion}}^{(4)}$	147.961(1)	154.704(2)	156.818(2)	152.376(5)	169.69(1)	180.822(8)	185.226(2)	178.461(3)	177.060(7)	215.696(5)
$E_{\text{ion}}^{(\text{CBS})}$	148.10	155.32	156.63	151.99	169.94	181.16	184.59	178.07	177.69	216.32
E_{expt}	151.32	157.47	155.25	156.04	171.48	182.27	181.47	175.12	178.17	216.63

yields need only be extrapolated before being used directly in calculating the IPs accurately, avoiding the need for composite approaches.

Methodological overview.—The full details of the i -FCIQMC method have been expounded elsewhere [24,28–32], and the following represents only a brief summary.

Beginning with a single, signed walker on the Hartree-Fock determinant, an iterative algorithm of “spawning,” “death,” and annihilation steps builds up an ensemble of walkers on excited determinants throughout the Hilbert space, such that the coefficients $\{C_i\}$ of a wave function are represented by the signed sum of those walkers on each determinant $|D_i\rangle$ in the space. The initial growth of walkers is exponential, but this can be stabilized by allowing a population-control parameter μ (which also provides an energy estimator) to vary. As in previous studies [24,33], we find here that a total walker population such that the number residing on the leading determinant, $N_0 = 50\,000$, is generally suitable to ensure that any systematic error is small. Once the ensemble has equilibrated, the simulation is allowed to evolve in imaginary time until the statistical errors in both μ and a projected-energy estimator E_{proj} have been satisfactorily reduced and perform a Flyvbjerg-Petersen blocking analysis to estimate the error in the obtained result [34].

The final point to note here is that spin-orbit coupling effects have not been included in these calculations. The experimental values to which we compare have, therefore, been removed of the effects of spin-orbit coupling and reflect the j -averaged values using experimental splittings [35–39].

Frozen-core calculations.—Complete-basis-set limit ionization potentials are computed as the difference between the separately extrapolated energies [40] of the neutral and cationic species: $E_{\text{ion}}^{(\text{CBS})} = E_{N-1}^{(\text{CBS})} - E_N^{(\text{CBS})}$. These extrapolations, of the inverse-cube, two-point type [41,42], are performed on the correlation energies, with the extrapolated value then added to the corresponding Hartree-Fock energy in the $X = 5$ basis. We begin by

correlating only the $4s$ and $3d$ electrons, holding the lower-lying 18-electron core frozen.

Apart from the very heaviest of these atoms, Cu and Zn, whose semicore electrons are rather corelike and thus contribute only weakly to the overall correlation, the ionization potentials achieved in Table I are not within chemical accuracy (taken to be within ± 1 kcal/mol) of the experimental values. The trend in the errors in these calculations compared to the experimental results, however, does bear qualitative agreement with that observed in valence-only coupled-cluster (CC) studies [21], suggesting that it is a product of genuine correlation effects and not some artefact of numerical error. It is clear, therefore, that, although these calculations are convenient and inexpensive to perform, a tractable means must be sought by which to

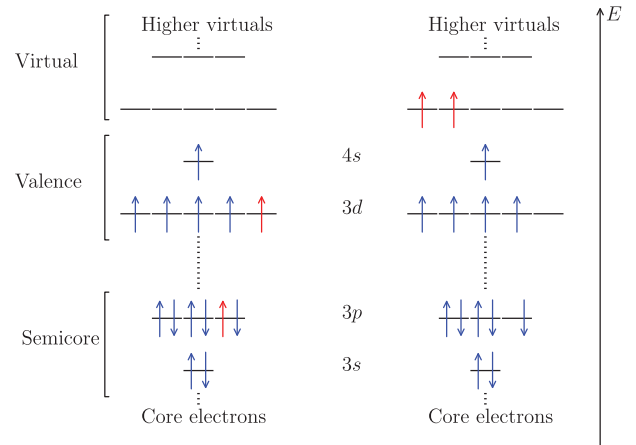


FIG. 1 (color). Schematic diagram of an allowed particle-hole excitation. On the left is shown the Hartree-Fock determinant (specifically, the Cr atom is illustrated), and on the right is an excited determinant in which the two “red” electrons have been promoted into the virtual manifold. One of these electrons is drawn from the $3p$ shell, and hence the determinant on the right would be admissible with $n_{h,3p} \geq 1$ but would be disallowed in the previous frozen-core regime. No such restriction is placed on electrons of the valence manifold.

TABLE II. Complete-basis-set limit ionization potentials in kcal/mol of the elements Sc to Ni with the allowed number of $3p$ holes, $n_{h,3p}$, compared to the experimental results [35–39].

System	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
$E_{\text{ion}}^{(\text{CBS})}(n_{h,3p} = 1)$	151.41	157.30	150.60	155.32	171.18	182.27	183.97	178.78
$E_{\text{ion}}^{(\text{CBS})}(n_{h,3p} = 2)$	151.07	157.31	157.91	156.64	171.54	182.38	186.06	179.78
$E_{\text{ion}}^{(\text{CBS})}(n_{h,3p} = 3)$	151.29	157.30	158.34	156.79	171.61	182.43	186.18	179.61
E_{expt}	151.32	157.47	155.25	156.04	171.48	182.27	181.47	175.12

treat core-valence effects, as has been suggested in previous studies [17,21].

Correlating the $3p$ manifold.—Correlating all of the $3p$ electrons entails such an increase in complexity that it has been found to pose computational difficulties for other high-level theories even in the smaller triple- ζ basis [21]. Such an expansion can, however, be avoided while still treating the semicore electrons. To achieve this, we expand the Hilbert space by including determinants in which some small number of holes, at most $n_{h,3p}$, may appear in the $3p$ shell—an approach which has been successful in other theories [43–45]. It is important to note that this approach does not simply allow excitations of $n_{h,3p}$ specific $3p$ electrons, but rather we allow excitations of any of the $3p4s3d$ manifold into the full virtual space, provided that at most $n_{h,3p}$ electrons are drawn from the $3p$ as illustrated in Fig. 1. As in the previous section, we perform two-point extrapolations to obtain $E_{\text{ion}}^{(\text{CBS})}$ for each atom at each level of semicore treatment.

The scale of the saving in terms of Hilbert space size (accounting for symmetry) is significant. Thus, for the Ni atom in the aug-cc-pVQZ-DK basis, the frozen-core space contains $O(10^{15})$ determinants, and a full treatment of the $3p$ manifold requires $O(10^{23})$. In contrast, the $n_{h,3p} = 1, 2,$ and 3 spaces contain $O(10^{16}), O(10^{17}),$ and $O(10^{19})$ determinants, respectively. Convergence was achieved in all the calculations of this section by using under 10^8 walkers. Increasing the hole number in the semicore manifold beyond two holes brings virtually no benefit in accuracy while substantially increasing the cost of the simulations.

As listed in Table II and illustrated in Fig. 2, this approach recovers chemically accurate ionization potentials for the majority of systems upon allowing a single $3p$ hole, with the values obtained converging upon increasing $n_{h,3p}$.

It is worth noting also that the ionization potentials which are successfully treated in this regime converge with respect to $n_{h,3p}$ from below, implying (since the method is variational) that, for a given element, there is comparatively more to be gained by treating the $3p$ electrons of the neutral atom than the cation. This we can rationalize by considering that the corelike electrons of the charged species are likely much more contracted than those in the corresponding neutral

species, and hence excitations therefrom play a much less prominent role in the overall description of the system.

Likewise, we may suggest why there is in general more to be gained by allowing a hole in a lighter atom than a heavier one. In the former case, the semicore electrons will be relatively less corelike, and hence one would expect their excitations to contribute more significantly to the FCI expansion. Indeed, previous work has stressed the importance of treating these effects in the cases of Sc and Ti [46], which prove difficult for effective core potential treatments even at the level of Hartree-Fock [47]. Conversely, the $3p$ electrons of, say, Fe and, in particular, Cu and Zn, are much more corelike, and very little extra correlation is captured in expanding the Hilbert space to include them.

Correlating the $3s3p$ manifold.—Though a treatment of the $3p$ manifold alone captures the correlation effects of the majority of systems, it is immediately clear from the upper panel of Fig. 2 that the three elements V, Co, and Ni, which have previously proven more challenging for *ab initio* methods [17,21], defy the general trend across the period. These are the three systems whose cations have a *greater*

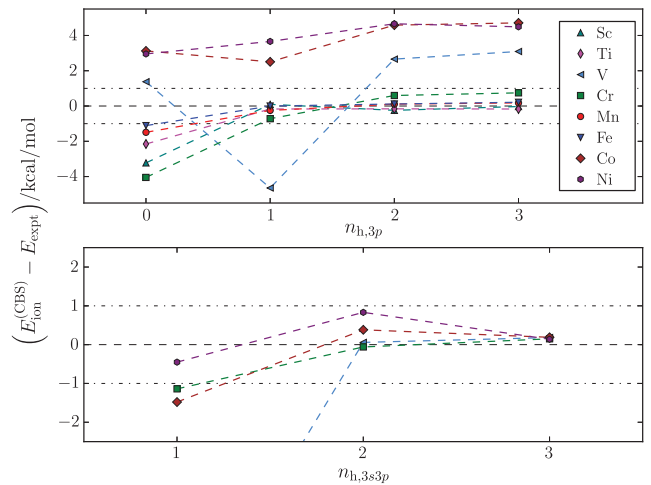


FIG. 2 (color). Convergence in complete-basis-set limit ionization potentials for the first-row transition-metal atoms compared to their experimental values with the allowed number of $3p$ holes, $n_{h,3p}$ (upper panel), and the allowed number of $3s3p$ holes, $n_{h,3s3p}$ (lower panel). Note that the $3s3p$ results for Co and Ni are achieved with Q5 extrapolations, while TQ extrapolations suffice for the remainder.

TABLE III. Complete-basis-set limit ionization potentials in kcal/mol of the elements V, Cr, Co, and Ni with the allowed number of $3s3p$ holes, $n_{h,3s3p}$. The TQ extrapolation (from aug-cc-pVTZ-DK and aug-cc-pVQZ-DK calculations) provides an adequate description for V and Cr, but a quintuple- ζ treatment is demanded by Co and Ni. As in previous tables, the experimental results are shown for comparison [17,21,35–39].

Extrapolation	System	V	Cr	Co	Ni	Cu	Zn
TQ	$E_{\text{ion}}^{(\text{CBS})}(n_{h,3s3p} = 1)$	147.38	154.90	180.46	175.32	178.08	216.71
	$E_{\text{ion}}^{(\text{CBS})}(n_{h,3s3p} = 2)$	155.31	155.98	182.93	176.14
	$E_{\text{ion}}^{(\text{CBS})}(n_{h,3s3p} = 3)$	155.43	156.19	182.78	176.20
Q5	$E_{\text{ion}}^{(\text{CBS})}(n_{h,3s3p} = 1)$	180.00	174.67
	$E_{\text{ion}}^{(\text{CBS})}(n_{h,3s3p} = 2)$	181.84	175.95
	$E_{\text{ion}}^{(\text{CBS})}(n_{h,3s3p} = 3)$	181.66	175.26
	E_{expt}	155.25	156.04	181.47	175.12	178.17	216.63

$3d$ occupancy than their neutral atoms and zero $4s$ occupancy, which correspondingly require a treatment of both $3p$ and $3s$ manifolds, since these electrons interact most strongly with the $3d$ [2].

Within the framework we have already introduced, this treatment may be accomplished by stipulating that at most $n_{h,3s3p}$ electrons may be excited from the $3s3p$ shells while continuing to correlate the $4s3d$ levels fully. These larger spaces entail more expensive calculations than those of the previous section but are still comparatively modest when set against the notion of fully correlating the $3s3p4s3d$ electrons.

As shown in Table III, allowing up to two holes in this expanded subspace and making the usual extrapolation provides a satisfactory treatment for vanadium, with little gained upon allowing the third. It also improves the description of Cr and Cu, whose cations similarly have no $4s$ electrons, as well as the largest atom, Zn. However, while this trend in convergence is replicated for Co and Ni, the values obtained exceed the experimental result by over 1 kcal/mol. This discrepancy appears to be a function of extrapolating to the complete-basis-set limit from bases

which are too small, since these systems with comparatively many active electrons place greater demands upon the resolution of the basis set. Indeed, if we extrapolate to the complete-basis-set limit as in previous sections but with correlation energies obtained from aug-cc-pVQZ-DK and the larger aug-cc-pV5Z-DK basis, as shown in the latter part of Table III and illustrated in the lower panel of Fig. 2, then chemically accurate ionization potentials emerge.

Conclusions.—Chemically accurate ionization potentials have been obtained for the first-row transition-metal atoms with a mean absolute error of 0.126 kcal/mol via i -FCIQMC calculations and two-point extrapolations to the complete-basis-set limit, with Douglas-Kroll-Hess scalar relativistic effects included. Such calculations smoothly converge to their experimental values with respect to the maximum number of holes n_h in the semicore manifold which determinants in the Hilbert space are permitted to contain. In the majority of cases, it is sufficient to use the $3p$ electrons as this manifold, but those elements whose cations have greater $3d$ occupancy than their neutral species demand the addition of the $3s$ as well. Moreover, it is usually adequate to perform the basis-set extrapolation by using the $X = 3$ and 4 basis sets, but the number of comparatively active electrons present in the heavy atoms Co and Ni demand an $X = 5$ treatment, too. As summarized in Table IV, the present work establishes a new theoretical benchmark for the ionization potentials of the $3d$ atoms, significantly improving upon previously reported Monte Carlo [48], multireference, and state-of-the-art coupled cluster results [21]. Also of note is that, while CC methods achieve IPs with a composite approach of successive corrections to an initial calculation, the energies from the i -FCIQMC method in an appropriately chosen Hilbert space need only be extrapolated before being used directly. It is hoped, therefore, that this approach will provide the framework to extend the i -FCIQMC method to the study of the challenging $3d$ transition-metal dimers and molecules.

TABLE IV. Comparison of the MAEs of the calculated IPs using (nonrelativistic) variational (VMC) and diffusion Monte Carlo (DMC) [48] and relativistic multireference averaged coupled-pair functional (ACPF) [using both ACPF and CCSD(T) for the core-valence correction, ΔE_{cv}] [21], CCSD(T) [17], and state-of-the-art CC methods [21] to the present work.

Method	MAE (kcal/mol)
VMC	16.860
DMC	9.665
ACPF (ACPF- ΔE_{cv})	0.658
ACPF [CCSD(T)- ΔE_{cv}]	0.502
CCSD(T)	0.325
State-of-the-art CC	0.305
i -FCIQMC	0.126

The authors acknowledge Trinity College, Cambridge, the Royal Society, and EPSRC for funding. The work was supported by EPSRC under Grant No. EP/J003867/1. The calculations made use of the facilities of the Max Planck Society's Rechenzentrum Garching.

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