# Computer-predicted ionization energy of carbon within $1\,\mathrm{cm}^{-1}$ of the best experiment

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(Dated: 24th November 2018)

We show that we can predict the first ionization energy of carbon to within 0.994 cm⁻¹ of the experimental value. This is an improvement of more than a factor of 5 over the preceding best prediction in [Phys. Rev. A **81**, 022503] and comparable to the accuracies achieved for the smaller atoms up to boron. The sum of all error contributions in our calculations up to the fifth power of the fine structure constant is estimated to be at most 0.802 cm⁻¹, which yields our estimate of contributions in the sixth and higher powers to be: 0.994 ± 0.802 cm⁻¹.

In the last seven years, ionization energies (IEs) have been calculated with unprecedented precision for the Li atom [? ], Be atom [? ] and B atom [? ]. Tight variational bounds for non-relativistic ground state energies assuming a clamped, point-sized nucleus have reached 49 digits in units of Hartree for He [? ], 19 digits for Li [? ], 12 digits for Be [? ], and 11 digits for B [? ] (see Table **??**). Calculated IEs have been made in agreement with experiment to within $10^{-3}$ cm⁻¹ for $^7$Li, $10^{-1}$ cm⁻¹ for $^9$Be and 1 cm⁻¹ for $^{11}$B (see Table **??**).

For the C atom, before this present study, no high-precision calculation had been reported to predict an IE to within $\sim 1$ cm⁻¹ agreement with experiment. Table **??** shows that the method used for the smaller atoms up to boron has not had success for carbon. With twice as many variationally optimizable parameters, one fewer digit was obtained for the B atom than for the Be atom, which also suggests that it would be very difficult to variationally optimize a fully explicitly correlated wavefunction ansatz for atoms and molecules coming from the rest of the periodic table.

The best known variational bound for the non-relativistic, clamped, point-sized nucleus (NR,CPN) ground state energy for C was calculated in 2015 using fixed-node diffusion Monte Carlo (FN-DMC) with the nodes of the electronic wavefunction fixed at the locations of a CISD/cc-pV5Z wavefunction, and the statistical uncertainty based on the stochastic fluctuations was $\pm 20\ \mu E_{\mathrm{Hartree}}$ [? ]. However, the IE for C predicted by FN-DMC was in discrepancy with experiment by more than 40 cm⁻¹. In this paper, the approach we use to calculate the NR,CPN energy of the ground state of C is FCIQMC (full configuration interaction quantum Monte Carlo) with basis sets as large as aug-cc-pCV8Z. Table **??** shows that our NR,CPN energy is at least 76 $\mu E_{\mathrm{Hartree}}$

higher than the variational upper bound obtained from FN-DMC; but since in our approach, imperfections in the description of the wavefunction for the neutral atom are almost the same as in the cation, the individual errors almost completely cancel when calculating the energy difference. Therefore, with our approach we achieve agreement with experiment that is comparable to what has been seen with the explicitly correlated approach for atoms as big as (but not exceeding) boron.

After adding relativistic and quantum electrodynamics (QED) corrections, and corrections to the clamped nucleus approximation, we obtained an IE for the ground sate of C which is in only 0.994 cm⁻¹ disagreement with the best known experimental estimate. While this is not as impressive as the method of variationally optimizing parameters in an explicitly correlated wavefunciton ansatz has proven to be for Li and Be, the disagreement with experiment has the same order of magnitude as the latter approach for B (see Table **??**). We finally note that the approach used in this paper, of calculating FCIQMC on a basis set of non-explicitly correlated orbitals has successfully treated systems with far more electrons (transition metal atoms [? ], diatomics [? ], larger molecules such as butadiene [? ], and even solid state systems [? ]), so it is conceivable that the approach used in this paper may in the near future be able to determine (with fair accuracy) the IEs which at present remain experimentally elusive or poorly known. These include arsenic (whose experimental IE has an uncertainty of $\pm 2$ cm⁻¹), Pm, Pa, Fm, Md, No, Sg, Bh and Hs (whose IEs are only known based on extrapolations of other experimental data and have uncertainties between $\pm 140$ cm⁻¹ and $\pm 4000$ cm⁻¹), Rf and Db (whose IEs are only known from theoretical calculations), and Mt, Ds, Rg, Cn, Nh, Fl, Mc, Lv, Ts, and Og (for which no IE is given in NIST's most recent