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

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We show that we can predict the first ionization energy of carbon to within $0.994\,\mathrm{cm}^{-1}$ 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.

In the last seven years, ionization energies (IEs) have been calculated with unprecedented precision for the Li atom [1], Be atom [2] and B atom [3]. 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 [4], 19 digits for Li [5], 12 digits for Be [6], and 11 digits for B [3] (see Table I). Calculated IEs have been made in agreement with experiment to within $10^{-3}\,\mathrm{cm}^{-1}$ for $^7\mathrm{Li}$, $10^{-1}\,\mathrm{cm}^{-1}$ for $^9\mathrm{Be}$ and $1\,\mathrm{cm}^{-1}$ for $^{11}\mathrm{B}$ (see Table II).

For the C atom, before this present study, no high-precision calculation had been reported to predict an IE to within ~ 1 cm^{-1} agreement with experiment. Table I 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 $\pm 20\ \mu E_{\mathrm{Hartree}}$ [7]. However, the IE for C predicted by FN-DMC was in discrepancy with experiment by more than $40\,\mathrm{cm}^{-1}$. 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 I shows that our NR,CPN energy is at least 76 μE_{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 state of C which is in only $0.994\,\mathrm{cm}^{-1}$ 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 II). 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 [8], diatomics [9], larger molecules such as butadiene [10], and even solid state systems [11]), 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 $\pm 2\,\mathrm{cm}^{-1}$), Pm, Pa, Fm, Md, No, Sg, Bh and Hs (whose IEs are only known based on extrapolations of other experimental data and have

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uncertainties between $\pm 140\,\text{cm}^{-1}$ and $\pm 4000\,\text{cm}^{-1}$), 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 databases).

I. METHODOLOGY

We begin with our main result in Table III, which shows that our computer-predicted ionization energy comes mainly from the NR-CPN Hamiltonian. This energy was calculated in four stages which we describe in the sub-sections below: (A) We developed larger core-valence (CV) basis sets than previously available for carbon, (B) we calculated the 1- and 2-electron integrals in these basis sets, (C) we solved the NR,CPN Schrödinger equation at the FCI level in our finite-sized basis sets of two different sizes, and (D) we extrapolated the finite basis set results to estimate the energies at the **c**omplete **b**asis **s**et (CBS) limits. Finally, sub-section (E) describes how we added the corrections due to special relativity, QED, and due to the atom having an unclamped nucleus.

Table III. Summary of our main result. All energies are between the hyperfine centre of gravity (hcog) of $\text{C}(^3P)$ and the hcog of $\text{C}^+(^2P)$ so the experimental spin-orbit lowering of $12.672508\,\text{cm}^{-1}$ needs to be subtracted from all numbers to obtain the $\text{C}(^3P_0) \leftarrow \text{C}^+(^2P_{1/2})$ energy (see Supplemental Material). The experimental uncertainty is a 68% confidence interval, meaning that there is a 32% chance that the true energy is outside the range spanned by the uncertainty.

Hamiltonian		Ionization Energy $[\,\text{cm}^{-1}\,]$	(Calc - Obs) $[\,\text{cm}^{-1}\,]$
NR-CPN		90 863 037(800)	
X2C		-30.023(050)	
Breit & QED		-0.5	
DBOC		-0.5	
Total (theory)	Present	90 832.014	-0.994
Experiment	2017 [21]	90 833.008(009)	
Theory	2010 [22]	90 838.75	5.74
Theory	2017 [23]	90 840.16	7.15
Theory	2015 [7]	90 786.66	-46.35

A. Optimization of 'tight function' exponents for the aug-cc-pCV7Z and aug-cc-pCV8Z basis sets.

The largest basis sets known for C prior to this work were the (aug-cc-pVXZ, $X =$ 7,8,9) sets used by Feller in 2016 [24]. These basis sets did not contain 'tight' exponent functions for capturing the effects of the correlation

between the core $(1s^2, 2s^2)$ electrons and the valence electrons $(2p^2)$. The largest known basis set for carbon prior to this work including the CV (core-valence) correction was the aug-cc-pCV6Z [25] set. In this work we start by optimizing the 'tight' exponents for the CV correction to Feller's 2016 aug-cc-pV7Z and aug-cc-pV8Z basis sets, yielding the first aug-cc-pCV7Z basis set for carbon, and the first aug-cc-pCV8Z basis set known.

The final aug-cc-pCVXZ basis sets have X new tight functions of s-type, $X - 1$ of p-type, $X - 2$ of d-type, and so forth, up to the final i-type function for $X = 7$ and the final k-type function for $X = 8$. The jth exponent corresponding to a function of type L is named $\gamma_{X,L,j}$, and is assumed to follow an "even-tempered" model: $\gamma_{X,L,j} = \alpha_{X,L,j}\beta_{X,L,j}^{j-1}$.

In the non-linear optimization procedure to obtain $\alpha_{7,L,j}$ and $\beta_{7,L,j}$, the starting values were chosen to be the $\alpha_{6,L,j}$ and $\beta_{6,L,j}$ values that were already optimized in [25]. These were then treated as free parameters to minimize the difference between the frozen core and all-electron CISD energies of the carbon atom with all other exponent functions fixed. The `MOLPRO` program [26] was used to calculate the CISD energies, and the `L-BFGS-B` program of [27] was used to optimize the free parameters. The s-type functions were added first, then once they were optimized they were held fixed while the p-type functions were added and optimized. Then both the s- and p-type functions were held fixed while the d-type functions were added, and so on up to the single i-type function. The procedure for $X = 8$ was the same, except the procedure continued to k-type functions, and the starting values came from the newly optimized $X = 7$ case rather than the $X = 6$ case from [25]. `MOLPRO` does not support k-functions, so we calculated the CISD energy at three points using `GAUSSIAN` [28] and found the minimum using a quadratic fit.

The tight exponents optimized in this work for aug-cc-pCV7Z and aug-cc-pCV8Z are presented in the Supplemental Material.

B. Calculation of 1- and 2-electron integrals including k- and l- functions

The calculation of the 1- and 2-electron integrals for (aug)-cc-p(C)VXZ basis sets with $X \geq 7$ is not possible with most quantum chemistry packages, since very few software packages support k- and l- functions, but for first row elements, k-functions appear in $X = 7$ basis sets and l-functions appear when $X = 8$. To calculate these integrals, we have used a locally modified version of `MOLCAS 8.0` [29] which supports larger basis sets. The 1- and 2-electron integrals for C and C^+ were evaluated in the basis of the optimized CASSCF(6,5) and CASSCF(5,5) orbitals respectively, with the five active orbitals being the $1s$, $2s$, $2p_x$, $2p_y$ and $2p_z$ of the C atom/ion. This active space is the minimal active space including all electrons, that is able to provide balanced orbitals for the three degenerate states of the ^3P state of the C atom, or

Table I. Tight variational upper bounds for total electronic energies. For H, the listed energy is exact, since the Hartree energy unit is defined as twice this energy, and can be related to fundamental SI units through an analytic solution to the relevant Schrödinger equation. VO stands for variational optimization (parameters in a wavefunction ansatz are optimized in attempt to obtain the lowest possible energy). Hylleraas-Log indicates the use of Hylleraas functions supplemented with auxiliary log functions, and ECG(N) indicates the use of explicitly correlated Gaussians with N variationally optimizable parameters. FN-DMC stands for fixed node diffusion Monte Carlo.

		Total non-relativistic clamped point-nucleus (NR,CPN) energy [Hartree]	Method/Ansatz type	Reference	
H	1	-0.5	Analytic	1926 Schrödinger	
He	2	-2.903 724 377 034 119 598 311 159 245 194 404 446 696 925 309 838	VO/Hylleraas-Log	2006 Schwartz	[4]
Li	3	-7.478 060 323 910 134 843	VO/Hylleraas	2011 Wang	[5]
Be	4	-14.667 356 494 9	VO/ECG(4096)	2013 Puchalski	[2]
B	5	-24.653 867 537	VO/ECG(8192)	2015 Puchalski	[3]
C	6	-37.844 48(2)	FN-DMC	2015 Yang	[7]
C	6	-37.844 355 5(08)	FCIQMC/aug-cc-pCV8Z	Present work	-
C	6	−37.843 333	VO/ECG(1000)	2013 Bubin	[12]

Table II. The most precisely calculated ionization energies for the first 6 atoms, compared to the best known experimental measurements to date. The last column indicates that if aiming for the best precision, an experimental measurement is still the best way to obtain the energy for most atoms, but for Be, the energy has been obtained more precisely *in silico* than in any experiment to date. The value for carbon of 90 832.014 cm^{-1} was calculated in the present work.

Transition	Experiment [cm^{-1}]		Theory [cm^{-1}]		Calc - Obs [cm^{-1}]	$\left|\frac{\text{Calc - Obs}}{\text{Uncertainty in obs}}\right|$	More precise
[1]H H$^+\left(1^1S\right) \leftarrow$ H$\left(1^2S\right)$	-		109 678.771 743 07(10)	[a]			Theory
[4]He He$^+\left(1^2S\right) \leftarrow$ He$\left(1^1S\right)$	198 310.666 37(2)	[15]	198 310.665 07(1)	[16]	-0.001 3	65.00	Theory
[3]Li Li$^+\left(1^1S\right) \leftarrow$ Li$\left(2^2S\right)$	3 487.159 40(18)	[17]	43 487.159 0(8)	[18]	-0.000 4	2.22	Experiment
[9]Be Be$^+\left(2^2S\right) \leftarrow$ Be$\left(2^1S\right)$	75 192.64(6)	[19]	75 192.699(7)	[2]	0.059	0.98	Theory
[11]B B$^+\left(2^1S\right) \leftarrow$ B$\left(2^2P\right)$	66 928.036(22)	[20]	66 927.91(21)	[3]	-0.126	5.73	Experiment
[12]C C$^+\left(2^2P\right) \leftarrow$ C$\left(2^3P\right)$	90 833.008(009)	[21]	90 832.014	-	0.994	110.44	Experiment

[a] This number is based on the data in [13] although it is not explicitly written anywhere there. Two of the authors of [13] have presented the number in Table III of [14].

the ^2P state of the C$^+$ ion.

C. Calculation of NR-CPN energies in finite basis sets without truncating the possible excitation levels (FCIQMC)

A deterministic FCI (full configuration interaction) calculation for the 5e$^-$ C$^+$ ion in the aug-cc-pCV7Z basis set would require almost 55 TB of RAM, and for the neutral atom would require more. Therefore we use FCIQMC for all NR-CPN calculations. The method was introduced in [30], and we use the initiator method first described in [31], and the semi-stochastic method as described in [32]. The calculations are performed using the developer version of the software NECI [33].

Within a given Hamiltonian (in this case the NR-CPN Hamiltonian) and basis set, there are three sources of error in the FCIQMC energy calculations:

1. Trial wavefunction error (ΔE_{trial}), which ap-

proaches zero in the limit where the number of determinants used in the trial wavefunction approaches the number of determinants in the FCIQMC wavefunction;

2. Initiator error ($\Delta E_{\text{initiator}}$), which approaches zero in the limit where the number of walkers N_{walkers} gets sufficiently large; and

3. Stochastic error (ΔE_{stoch}), which for a given number of walkers is estimated as the square root of the unbiased variance among different estimates E_i of the energy from their mean $\bar{E}$ after different numbers N of Monte Carlo macro-iterations (determined using the Flyvbjerg-Petersen blocking analysis [34]) after the walkers have reached equilibrium:

$$\Delta E_{\text{stochastic}} \approx \sqrt{\frac{\sum_{i=1}^{N}\left(E_i - \bar{E}\right)^2}{N-1}} = \mathcal{O}\left(1/\sqrt{N}\right).$$

Our goal was to obtain all energies to a precision of

$\pm\epsilon$ where $\epsilon \le 1\mu E_{\text{Hartree}} \approx 0.2$ cm^{-1} (within the basis sets used). To ensure that $\Delta E_{\text{initiator}}$ can be neglected, we used a sufficiently large value of N_{walkers} for every energy calculation, so that the energy difference between using N_{walkers} and $\frac{1}{2}N_{\text{walkers}}$ was smaller than $1\ \mu E_{\text{Hartree}}$. Likewise, to ensure that ΔE_{trial} can be neglected, we used a sufficiently large number of determinants in the trial wavefunction for every energy calculation, such that ΔE_{trial} would also be smaller than $1\ \mu E_{\text{Hartree}}$. We then ran every calculation for enough macro-iterations N such that ΔE_{stoch} was smaller than ΔE_{trial} and $\Delta E_{\text{initiator}}$. Further details are presented in the Supplemental Material, including tables which show that all three sources of error in our final numbers are not larger than we claim.

Table IV. Final NR-CPN energies. The break-down of how these energies were obtained, and the Hartree-Fock energies that were used for the extrapolations are available in the Supplemental Material. Numbers in parenthesis indicate uncertainties in the last digit(s) shown, and their determination is described in the Supplemental Material.

	C(^3P) [E_{Hartree}]	C$^+$(^2P) [E_{Hartree}]	$2^3P \to 2^2P$ [cm^{-1}]
aug-cc-pCV7Z	-37.844 251 5(05)	-37.430 345 1(01)	90 841.955(028)
aug-cc-pCV8Z	-37.844 355 5(08)	-37.430 412 5(05)	90 849.987(054)
Eq.(3), $n = 3.5$	-37.844 528 6	-37.430 523 6	90 863.604
Eq.(4), $n = 4$	-37.844 514 2	-37.430 514 3	90 862.471
Mean (σ)	-37.844 521 4	-37.430 519 0	90 863.037

D. Extrapolations to the CBS (complete basis set) limit

We use two different families of formulas to extrapolate the correlation energies (FCIQMC energies with the ROHF energies subtracted out) from E_{X-1} and E_X to E_{CBS}:

$$E_{\text{CBS}} = E_X - \frac{A}{X^n}\ , \tag{1}$$

$$E_{\text{CBS}} = E_X - \frac{A}{(X + 1/2)^n}\ . \tag{2}$$

If we set $n = 3$ in Eq.(1), we recover the formula originally proposed in [35]. If we set $n = 4$ in Eq.(2), we recover the formula originally proposed in [36]. If we have values for E_X at two different X values, we can eliminate A in both cases, so Eq.(1) leads to Eq.(3) and Eq.(2) leads to Eq.(4):

$$E_{\text{CBS}} = \frac{X^n E_X - (X-1)^n E_{X-1}}{X^n - (X-1)^n}\ , \tag{3}$$

$$E_{\text{CBS}} = E_X + \frac{(2X-1)^n (E_X - E_{X-1})}{(1+2X)^n - (2X-1)^n}\ . \tag{4}$$

As explained on page 5 of [24], extrapolations to the CBS limit using $n = 3$ in Eq.(1) tend to over-shoot the CBS limit. The value of $n = 3.5$ was therefore used in [24], and we have used it in this present study. The values of E_{CBS} obtained from using $n = 3.5$ in Eq.(3) and $n = 4$ in Eq.(4), for $X = 8$ were added to the ROHF energies for $X = 8$ and are presented in Table IV. The final NR-CPN energy was taken as the mean of both values obtained from extrapolating the correlation energy and adding it to the ROHF energy with $X = 8$, and the uncertainty in this mean was estimated as the square root of the unbiased variance of the two values.

E. Estimation of relativistic, QED, and finite nuclear mass corrections corrections

Scalar relativistic corrections were calculated by comparing the energies using the spin-free version of the 1e$^-$ X2C (exact 2-component) Hamiltonian, to the energies of the NR-CPN Hamiltonian. The integrals of our X2C Hamiltonian with ROHF orbitals were done in the CFOUR program, and were calculated at various levels of coupled cluster theory with the MRCC program [37].

Further scalar relativistic effects were included by adding the Breit and QED corrections (including the vacuum polarization and the self-energy terms that together comprise the Lamb shift) from the state-averaged Dirac-Fock calculations done in [22]. The overall contribution from the Breit and QED correctons to the IE for C was -0.48 cm^{-1}.

Diagonal Born-Oppenheimer breakdown corrections (DBOC) to the clamped nucleus approximation were calculated using CFOUR, with MRCC used for the coupled-cluster part. Our value of -0.50 cm^{-1} is more than double the value of -0.08 cm^{-1} estimated in [22], due to including higher levels of correlation.

The basis set and correlation convergence of the X2C and DBOC corrections is shown in the Supplemental Material and the final corrections that contributed to our final computer-predicted ionization energy are presented in Table III.

II. CONCLUSION

Table III summarizes the various contributions to our value of the IE, and compares our final value to experiment and to three recent theoretical estimates. Our value is 0.994 cm^{-1} smaller than the best experimental value.

The best theoretical estimate of the IE before this work was in [22], and was in disagreement with experiment by more than a factor of 5 more than our present result. We believe that this could have been due to any or all of three things: (1) approximations inherent to the F12 approach used for their NR-CPN energy, (2) the perturbative nature of their scalar relativistic corrections (i.e. use the mass velocity and Darwin terms, rather than the X2C Hamiltonian used in the present work) and (3) the CCSD approximation made in their DBOC correction (as opposed to the CCSDTQ used in the present work which we have shown appears to be converged to the FCI limit).

[1] M. Puchalski, D. Kędziera, and K. Pachucki, Phys. Rev. A **82**, 062509 (2010).

[2] M. Puchalski, J. Komasa, and K. Pachucki, Physical Review A **87**, 030502 (2013).

[3] M. Puchalski, J. Komasa, and K. Pachucki, Physical Review A **92**, 062501 (2015).

[4] C. Schwartz, ArXiv Mathematical Physics e-prints (2006), math-ph/0605018.

[5] L. M. Wang, Z.-C. Yan, H. X. Qiao, and G. W. F. Drake, Phys. Rev. A **83**, 034503 (2011).

[6] M. Puchalski, D. Kedziera, and K. Pachucki, Physical Review A **87**, 032503 (2013).

[7] Y. Yang, I. Kylänpää, N. M. Tubman, J. T. Krogel, S. Hammes-Schiffer, and D. M. Ceperley, The Journal of Chemical Physics **143**, 124308 (2015).

[8] R. E. Thomas, G. H. Booth, and A. Alavi, Physical Review Letters **114**, 033001 (2015).

[9] D. Cleland, G. H. Booth, C. Overy, and A. Alavi, Journal of Chemical Theory and Computation **8**, 4138 (2012).

[10] C. Daday, S. Smart, G. H. Booth, A. Alavi, and C. Filippi, Journal of Chemical Theory and Computation **8**, 4441 (2012).

[11] G. H. Booth, A. Grüneis, G. Kresse, and A. Alavi, Nature **493**, 365 (2012).

[12] S. Bubin, M. Pavanello, W.-C. Tung, K. L. Sharkey, and L. Adamowicz, Chemical Reviews **113**, 36 (2013).

[13] U. D. Jentschura, S. Kotochigova, E.-O. Le Bigot, P. J. Mohr, and B. N. Taylor, Phys. Rev. Lett. **95**, 163003 (2005).

[14] P. J. Mohr, D. B. Newell, and B. N. Taylor, Rev. Mod. Phys. **88**, 035009 (2016).

[15] D. Z. Kandula, C. Gohle, T. J. Pinkert, W. Ubachs, and K. S. E. Eikema, Physical Review A **84**, 062512 (2011).

[16] K. Pachucki, V. Patkóš, and V. A. Yerokhin, Physical Review A **95**, 062510 (2017).

[17] B. A. Bushaw, W. Nörtershäuser, G. W. F. Drake, and H.-J. Kluge, Phys. Rev. A **75**, 052503 (2007).

[18] M. Puchalski and K. Pachucki, Physical Review A **78**, 052511 (2008).

[19] R. Beigang, D. Schmidt, and P. J. West, Le Journal de Physique Colloques **44**, C7 (1983).

[20] A. E. Kramida and A. N. Ryabtsev, Physica Scripta **76**, 544 (2007).

[21] K. Haris and A. Kramida, (2017), arXiv:1704.07474.

[22] W. Klopper, R. A. Bachorz, D. P. Tew, and C. Hättig, Phys. Rev. A **81**, 022503 (2010).

[23] D. Feller, The Journal of Chemical Physics **147**, 34103 (2017).

[24] D. Feller, The Journal of Chemical Physics **144**, 014105 (2016).

[25] A. K. Wilson, T. van Mourik, and T. H. Dunning, Journal of Molecular Structure: THEOCHEM **388**, 339 (1996).

[26] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and M. Wang, "Molpro, version 2015.1, a package of ab initio programs," (2015), see http://www.molpro.net.

[27] C. Zhu, R. H. Byrd, P. Lu, and J. Nocedal, ACM Trans. Math. Softw. **23**, 550 (1997).

[28] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, "Gaussian 16 Revision A.03," (2016), Gaussian Inc. Wallingford, CT.

[29] F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. Fdez. Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. Li Manni, H. Lischka, D. Ma, P.-Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata, and R. Lindh, Journal of Computational Chemistry **37**, 506 (2016).

[30] G. H. Booth, A. J. W. Thom, and A. Alavi, The Journal of Chemical Physics **131**, 054106 (2009).

[31] D. Cleland, G. H. Booth, and A. Alavi, The Journal of Chemical Physics **132**, 041103 (2010).

[32] N. S. Blunt, S. D. Smart, J. A. F. Kersten, J. S. Spencer, G. H. Booth, and A. Alavi, The Journal of Chemical Physics **142**, 184107 (2015).

[33] "Public version is available here: `https://github.com/ghb24/NECI_STABLE`.".

[34] H. Flyvbjerg and H. G. Petersen, The Journal of Chemical Physics **91**, 461 (1989).

[35] W. Kutzelnigg and J. D. Morgan, The Journal of Chemical Physics **96**, 4484 (1992).

[36] J. M. Martin, Chemical Physics Letters **259**, 669 (1996).

[37] M. Kallay, Z. Rolik, J. Csontos, P. Nagy, G. Samu, D. Mester, I. Ladjanszki, L. Szegedy, B. Ladoczki, K. Petrov, M. Farkas, and B. Hegely, "MRCC, a quantum chemical program suite.".