

Article

Towards Chemical Accuracy in Atomic Ionization Energies: The Case of H, C, N, O, F, P, and S Atoms

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Abstract

Accurate ionization energies are essential for understanding the electronic structures of atoms and molecules and benchmarking quantum-chemical methods. We report the calculated ionization energies of the H, C, N, O, F, P, and S atoms using several quantum-chemical approaches, aiming at reproducing the experimental values within chemical accuracy. The methods include the electron propagator approximations OVGF and P3+, the coupled-cluster methods CCSD(T), CCSDT, and IP-EOM-CCSD, and the composite methods G3 and CBS-QB3. The CCSD(T), CCSDT, G3, and CBS-QB3 methods, together with the DFT method with B2PLYP density functional and several post-Hartree–Fock methods, were used in conjunction with the energy-difference approach. The coupled-cluster calculations were combined with the aug-cc-pVXZ-DK, aug-cc-pVXZ, and ANO-RCC basis sets, all-electron correlation, DKH2 scalar relativistic corrections, atomic spin-orbit corrections, and extrapolation to the complete basis set (CBS) limit. The OVGF and P3+ methods do not achieve chemical accuracy on average, while CCSD(T) and CCSDT combined with the aug-cc-pVXZ-DK basis set and CBS extrapolation reach mean absolute errors of 0.0030 and 0.0026 eV, respectively, an order of magnitude below the chemical accuracy threshold. CCSD(T)/aug-cc-pVXZ-DK with CBS extrapolation provides the best compromise between accuracy and computational cost and can be used as a reference atomic benchmark for these ionization energies.

Keywords: atomic ionization; OVGF; P3+; CCSD(T); IP-EOM-CCSD; CBS extrapolation; DKH2; chemical accuracy



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1. Introduction

The calculation of ionization energies of atoms may be useful for understanding electron-removal processes, for benchmarking quantum-chemical methods, and for evaluating the electronic structure of neutral and cationic species. Isolated atoms provide simple and well-defined benchmark systems because their ionization energies can be directly compared with accurate experimental reference values and are not affected by molecular geometry, vibrational effects, or environmental interactions. For this reason, atomic ionization energies and related atomic properties have been used in previous benchmark studies of density functional and wave function methods [1,2].

Two types of ionization energy (i.e., vertical and adiabatic) can be defined for molecular systems. The vertical ionization energy assumes that, during the removal of an electron, the geometry of the system remains unchanged. By contrast, in the case of the adiabatic ionization energy, the geometry of the ionized species is allowed to relax after the electron

removal. Experimentally, ionization energies can be determined, for example, by photoelectron spectroscopy [3], from the difference between the energy of the incident photons and the kinetic energy of the emitted photoelectrons. For isolated atoms, the distinction between vertical and adiabatic ionization energies does not apply in the same way as for molecules, because no molecular geometry relaxation is involved. In this case, the ionization energy is given by the energy difference between the cation and the corresponding neutral atom.

We computed the ionization energies of several atoms commonly found in proteins, namely H, C, N, O, and S, as well as two additional atoms, F and P. The atoms H, C, N, O, and S are present in essential amino acids, while the atoms F and P may occur in synthetic amino acids and exhibit properties that can be exploited in the pharmaceutical industry [4,5]. Because fluorine is the most electronegative element, it forms strong bonds with carbon and can therefore be used in protein engineering for the synthesis of highly stable proteins [6]. Phosphorus-containing amino acids also have a variety of applications. For example, they may act as protecting groups, serve as antiviral agents incorporated into prodrugs, or be used for ^{18}F labeling [7,8].

The methods employed in this work to compute ionization energies include the energy-difference approach and the electron propagator theory (EPT) methods, namely the Outer Valence Green's Function (OVGF) and the renormalized partial third-order quasiparticle (P3+) methods. The energy-difference approach was combined with the B2PLYP DFT method and various post-Hartree–Fock methods. In addition, the coupled-cluster methods CCSD(T), CCSDT, and IP-EOM-CCSD were employed, in conjunction with aug-cc-pVXZ-DK, aug-cc-pVXZ, and ANO-RCC basis set families, with all-electron correlation treatment, the second-order Douglas–Kroll–Hess (DKH2) scalar relativistic Hamiltonian, and extrapolation to the complete basis set (CBS) limit using the two-point Helgaker formula. The aim of these calculations was to achieve chemical accuracy, defined here as a maximum deviation of 1 kcal/mol between the experimental and calculated ionization energies (1 kcal/mol = 4.184 kJ/mol = 0.0434 eV) [9]. The results obtained in this study provide an elemental benchmark for the theoretical methods investigated here.

2. Computational Methods

In the energy-difference approach, the ionization potential is obtained as the energy difference between the cation, generated by removing one electron, and the corresponding neutral system [10]:

$$I = E_{\text{cation}} - E_{\text{neutral}} \quad (1)$$

To obtain the adiabatic ionization energy, both the neutral system and the cation are optimized, and the difference between their total energies is then evaluated. By contrast, the vertical ionization energy is obtained by calculating the energy of the cation at the geometry of the neutral system. The approach was previously used by Jursic [11] to compute the ionization potentials of several second-row elements (C, N, O, F) employing DFT and ab initio methods.

The electron propagator theory (EPT) [12] is a useful framework for the calculation of ionization energies, electron affinities, one-electron properties, and spectral intensities. EPT is based on the concept of a propagator. For an electron in a quantum system, the propagator is given by the expectation value of the time-evolution operator between the initial and final states,

$$G(\vec{r}_i, \vec{r}_f, t, t') = \langle \vec{r}_f | \hat{U}(t, t') | \vec{r}_i \rangle \quad (2)$$

where $\hat{U}(t, t')$ is the time evolution operator. The one-particle Green's function [13] can be used to calculate electron propagators. EPT is based on the solution of the Dyson equation [14–16],

$$G = G^0 + G^0 \Sigma G \quad (3)$$

where G is the one-particle Green's function, G^0 is the free Green's function, and Σ is the self-energy which contains the correlation and final-state relaxation effects [17,18]. The Dyson equation may be transformed into the following one-electron equation [18–20]:

$$[F + \Sigma(E)]\phi^{Dyson} = E\phi^{Dyson} \quad (4)$$

where F is the one-electron Fock operator, E is the energy, and ϕ^{Dyson} is the Dyson orbital [21]. The Dyson orbital corresponding to the ionization from the initial state $\Psi_N(x_1, \dots, x_N)$ to the final state $\Psi_{s,N-1}(x_2, \dots, x_N)$ is defined as [19]:

$$\phi_s^{Dyson}(x_1) = \sqrt{N} \int \Psi_N(x_1, x_2, \dots, x_N) \Psi_{s,N-1}^*(x_2, x_3, \dots, x_N) dx_2 dx_3 \dots dx_N \quad (5)$$

where x_i stands for the space-spin coordinate of electron i .

Based on the Dyson orbital, the pole strength, which takes values in the $[0, 1]$ interval, can be computed as follows [20,21]:

$$p_s = \int |\phi_s^{Dyson}(x)|^2 dx \quad (6)$$

For strong correlation, the pole strength is close to zero, whereas for weak correlation, it approaches unity [18]. When the Koopmans picture provides a qualitatively valid description of the Ψ_N and $\Psi_{s,N-1}$ states, the pole strength is greater than 0.85 [18].

In this paper, we employ two diagonal approximations of the EPT, namely OVGf and P3+, in which the off-diagonal elements of the self-energy matrix are neglected [22]. The OVGf method is designed for outer valence electrons and is based on a perturbative expansion of the self-energy that is exact through third order, while higher-order contributions are treated approximately [16]. There are three variants of the OVGf method, denoted A, B, and C, which differ in the form of self-energy expression. The corresponding expressions for self-energy are given in ref. [12]. Method A is applied when the ionization energy is greater than 15 eV, whereas method B is used when the ionization energy is smaller than 15 eV [22]. Approximations A and B correspond to the cases in which the second-order terms in the self-energy exceed the third-order terms, whereas approximation C is used when the second-order terms are small [22]. An algorithm for selecting between methods A, B, and C is listed in ref. [22]. The computational costs of the OVGf method scale as OV^4 , where O is the number of occupied orbitals and V is the number of virtual orbitals [17,18,23]. For closed-shell systems, the absolute error in computed vertical ionization potential below 20 eV is about 0.25 eV [22,24].

The P3 method [25] neglects some terms from the self-energy expression used in OVGf. A renormalized version of P3, denoted P3+, has proven to be very effective for computing the ionization energies of challenging anions [19]. The computational cost of both P3 and P3+ scales as O^3V^2 , which represents an improvement over the OVGf method because the number of occupied orbitals is usually much smaller than the number of virtual orbitals [18]. For P3+, the mean absolute deviations of less than 0.2 eV between calculated and experimental ionization energies have been reported for anions with ionization potentials below 20 eV [19].

For the seven atoms considered in this work, the energy-difference approach was used in conjunction with the DFT functional B2PLYP [26], as well as the post-Hartree–Fock

methods MP2 [27], CCSD(T) [28,29], QCISD(T) [29], G3 [30], and CBS-QB3 [31]. These methods were combined with the aug-cc-pVQZ basis set. The OVGF and P3+ calculations were performed with the 6-311+G(2df,p), cc-pVQZ, and aug-cc-pVQZ basis sets. All these calculations were carried out with Gaussian 16 Revision C.01 [32] on the High-Performance Computing Center of Babeş-Bolyai University [33].

In addition to the calculations described above, the coupled-cluster methods CCSD(T) [28,29], CCSDT [34], and IP-EOM-CCSD [35,36] were used for the calculation of the ionization energies of the C, N, O, F, P, and S atoms, as implemented in ORCA 6.1.0 [37]. The CCSD(T) method combines the iterative coupled-cluster treatment of single and double excitations with a perturbative correction of the triple excitations. The CCSDT method provides an iterative treatment of the triple excitations and was employed in order to evaluate the quality of the perturbative correction in the CCSD(T). The CCSDT calculations were performed using the *AUTOCl* module implemented in ORCA. The IP-EOM-CCSD method is an equation-of-motion (EOM) coupled-cluster approach for ionization energies. It is based on a neutral CCSD reference state, while the ionized states are described through electron removal operators in the EOM space. Therefore, unlike the energy-difference approach, IP-EOM-CCSD gives the ionization energies directly. For the hydrogen atom, which is a one-electron system, only Hartree–Fock (HF) calculations were performed.

For all ORCA 6.1.0 calculations, the *VeryTightSCF* convergence criterion was used, which corresponds to a total energy change between consecutive iterations below 10^{-9} Hartree, a maximum density matrix change below 10^{-8} , and an RMS density matrix change below 10^{-9} . For all Gaussian 16 calculations, the default SCF convergence criterion was used, which corresponds to the *Tight* criterion and to an RMS density matrix change below 10^{-8} and a maximum density matrix change below 10^{-6} .

Three families of basis sets were used: the aug-cc-pVXZ basis sets ($X = Q, 5$) [38,39], the corresponding relativistically recontracted aug-cc-pVXZ-DK basis sets ($X = Q, 5$) [40], and the relativistically contracted atomic natural orbitals basis sets (ANO-RCC) at the TZP, QZP, and Full contraction levels [41]. The aug-cc-pVXZ-DK and ANO-RCC calculations were performed in conjunction with the second-order Douglas–Kroll–Hess scalar relativistic Hamiltonian (DKH2) [42,43] and the finite nucleus model, while the aug-cc-pVXZ calculations were performed without relativistic corrections. All electrons were included in the correlation treatment through the *NoFrozenCore* option. For the CCSD(T) and CCSDT calculations, the ionization energies were obtained as the energy differences between the neutral and cationic atoms. For the IP-EOM-CCSD calculations, the ionization energies were obtained directly from the ionized roots of the neutral reference state. For the six atoms with more than one electron, the α and β electron removal roots were treated separately, and the first ionization energy was considered to be the lower value.

In order to reduce the basis set error, the ionization energies obtained with CCSD(T), CCSDT, and IP-EOM-CCSD were extrapolated to the complete basis set (CBS) limit using the two-point formula of Helgaker et al. [44,45]:

$$E_X = E_{CBS} + \frac{A}{X^3} \quad (7)$$

which results in

$$E_{CBS} = \frac{Y^3 E_Y - X^3 E_X}{Y^3 - X^3} \quad (8)$$

where X and Y are the cardinal numbers of the basis sets used in the extrapolation. For the aug-cc-pVXZ-DK and aug-cc-pVXZ basis sets, the (Q, 5) pair was used, while for the ANO-RCC basis sets, the (T, Q) pair was employed based on the TZP and QZP contractions. For the CCSD(T) and CCSDT methods, a dual-level CBS extrapolation scheme was used, in

which the total energy at each basis set level was separated into a self-consistent field (SCF) component and a correlation component:

$$E_{tot}(X) = E_{SCF}(X) + E_{corr}(X) \quad (9)$$

This separation was justified by the fact that the two contributions exhibit different convergence patterns as the basis set size increases [45,46]. The SCF energy converges exponentially with the cardinal number and is already close to the CBS limit at the 5Z level, while the correlation energy converges asymptotically with X^{-3} . Therefore, the ionization energy at the CBS limit was obtained as:

$$IE_{SCF}(Y) = E_{SCF}^{cat}(Y) - E_{SCF}^{neu}(Y) \quad (10)$$

$$IE_{corr}(X) = E_{corr}^{cat}(X) - E_{corr}^{neu}(X) \quad (11)$$

$$IE_{corr,CBS} = \frac{Y^3 IE_{corr}(Y) - X^3 IE_{corr}(X)}{Y^3 - X^3} \quad (12)$$

$$IE_{CBS} = IE_{SCF}(Y) + IE_{corr,CBS} \quad (13)$$

where $Y = X + 1$ and the SCF contribution is taken from the larger basis set, namely aug-cc-pV5Z, aug-cc-pV5Z-DK, and ANO-RCC-QZP. This scheme was used by Richard et al. [46] for the calculation of ionization potentials and electron affinities at the CCSD(T)/CBS limit. For the IP-EOM-CCSD method, which computes the ionization energy directly, the extrapolation was applied directly to the α and β electron removal ionization energies [47]:

$$IE_{s,CBS} = \frac{Y^3 IE_s(Y) - X^3 IE_s(X)}{Y^3 - X^3}, \quad s = \alpha, \beta \quad (14)$$

The first ionization energy at the CBS limit was then obtained as the lower of the two extrapolated values.

The calculations described above are scalar-relativistic and therefore do not include spin–orbit coupling (SOC) explicitly. Consequently, the calculated atomic energies correspond to the spin-free LS terms, whereas the experimental ionization energies used as reference values [48] are defined between the lowest fine-structure level of the neutral atom and the lowest fine-structure level of the corresponding cation. In order to allow a direct comparison with the experimental values, atomic SOC corrections were derived from the fine-structure levels reported in the NIST Atomic Spectra Database [48], following the procedure commonly used in high-accuracy thermochemistry protocols and thermochemical spin–orbit corrections [49–51].

For each LS term, the E_{LS} value was calculated from the fine-structure levels as a degeneracy-weighted average, using the corresponding $(2J + 1)$ statistical weights [51]:

$$E_{LS} = \frac{\sum_J (2J + 1) E_J}{\sum_J (2J + 1)} \quad (15)$$

The SOC stabilization of the ground level (ΔE_{SO}) was defined as the energy difference between E_{LS} and the lowest fine-structure level:

$$\Delta E_{SO} = E_{LS} - E_{J(lowest)} \quad (16)$$

The SOC contribution to the ionization energy was then obtained from the difference between the cationic and neutral ΔE_{SO} values:

$$\Delta IE_{SO} = \Delta E_{SO}^{cation} - \Delta E_{SO}^{neutral} \quad (17)$$

The SOC-corrected ionization energy was calculated as:

$$IE_{SO-corrected} = IE_{scalar} - \Delta IE_{SO} \quad (18)$$

The ΔE_{SO} and ΔIE_{SO} values obtained for each atom are reported in Table S1. These corrections were applied to all theoretical ionization energies except the G3 and CBS-QB3 results. The composite methods already include spin–orbit correction terms; thus, no additional SOC correction was applied to their final energies. Therefore, all ionization energies reported in the following tables can be directly compared with the NIST experimental reference values.

3. Results and Discussion

3.1. Ionization Energies for the C, N, O, F, P, and S Atoms Obtained with the OVGF and P3+ Methods

Table 1 summarizes the ionization energies of the six atoms C, N, O, F, P, and S calculated using the OVGF and P3+ methods. The hydrogen atom was not considered within these approaches because, having only one electron, electron correlation is absent. Three basis sets were used: cc-pVQZ, aug-cc-pVQZ, and 6-311+G(2df,p). The table reports both the experimental ionization energies and the values computed with the OVGF and P3+ methods. For OVGF, the A, B, and C variants were considered according to the algorithm implemented in the Gaussian package, and the selected variants are reported in Table 1 for each atom and basis set combination. For all three basis sets, variant B was selected for the C, N, and O atoms, variant A for the F atom, and variant C for the P and S atoms. This selection is consistent with the criteria reported in ref. [22], based on the magnitude of the second-order and third-order self-energy contributions. Besides these quantities, the table includes the spin multiplicities of the neutral atoms, the indexes of the HOMO and LUMO orbitals, and the orbital window employed in the calculations.

Table 1. Calculated values with the OVGF and P3+ methods for the ionization energies of the C, N, O, F, P, and S atoms, with different basis sets.

Atom	IE _{exp} (eV) [48]	Basis Set	Multiplicity	IE _{OVGF} Recomm.	IE _{OVGF} (eV)	ΔIE _{OVGF} (eV)	IE _{P3+} (eV)	ΔIE _{P3+} (eV)	HOMO/ LUMO	Orbital Window
C	11.2603	cc-pVQZ	3	B	11.3741	0.1138	11.1644	−0.0959	2a/4a	1-6
		aug-cc-pVQZ	3	B	11.3858	0.1255	11.1744	−0.0859		
		6-311+G(2df,p)	3	B	11.3555	0.0952	11.1094	−0.1509		
N	14.5341	cc-pVQZ	4	B	14.6153	0.0812	14.3740	−0.1601	2a/2b	1-6
		aug-cc-pVQZ	4	B	14.6433	0.1092	14.3920	−0.1421		
		6-311+G(2df,p)	4	B	14.6168	0.0827	14.3200	−0.2141		
O	13.6181	cc-pVQZ	3	B	13.5740	−0.0441	13.2387	−0.3794	2b/3b	1-5
		aug-cc-pVQZ	3	B	13.6361	0.0180	13.2847	−0.3334		
		6-311+G(2df,p)	3	B	13.5036	−0.1145	13.1087	−0.5094		
F	17.4228	cc-pVQZ	2	A	17.2979	−0.1249	17.0529	−0.3699	2b/4b	1-5
		aug-cc-pVQZ	2	A	17.3841	−0.0387	17.1179	−0.3049		
		6-311+G(2df,p)	2	A	17.2873	−0.1355	16.9489	−0.4739		
P	10.4867	cc-pVQZ	4	C	10.4577	−0.0290	10.3839	−0.1028	2a/2b	1-5
		aug-cc-pVQZ	4	C	10.4748	−0.0119	10.3899	−0.0968		
		6-311+G(2df,p)	4	C	10.4115	−0.0752	10.3109	−0.1758		
S	10.3600	cc-pVQZ	3	C	10.2452	−0.1148	10.1113	−0.2487	2b/3b	1-7
		aug-cc-pVQZ	3	C	10.2719	−0.0881	10.1303	−0.2297		
		6-311+G(2df,p)	3	C	10.0860	−0.2740	9.9343	−0.4257		

Figure 1 sketches the atomic orbital levels of the C, N, O, F, P, and S atoms used in the OVGF calculations, while Figure 2 exemplifies the orbital indexing for the OVGF method in the case of the sulfur atom.

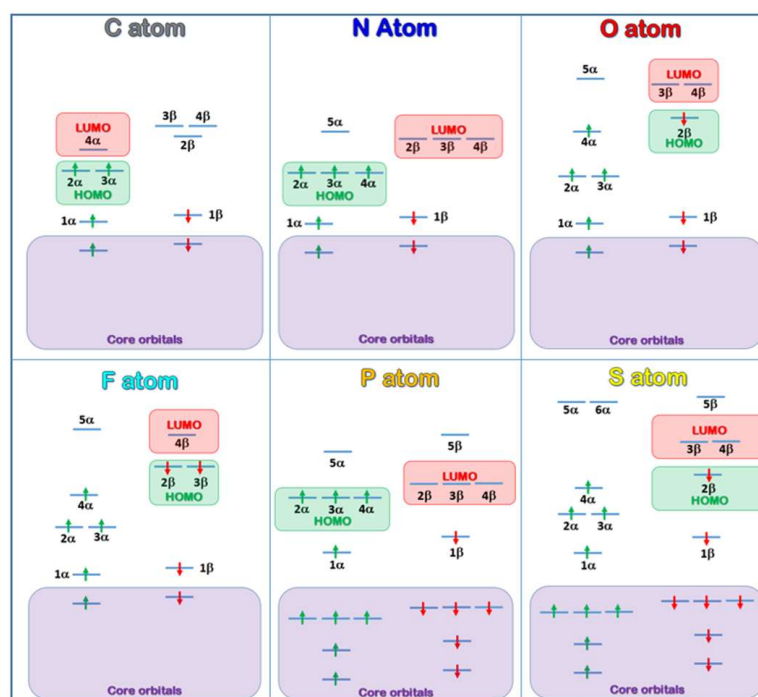


Figure 1. Schematic representation of the atomic orbitals of C, N, O, F, P, and S for ionization energy calculations using the OVGf method.

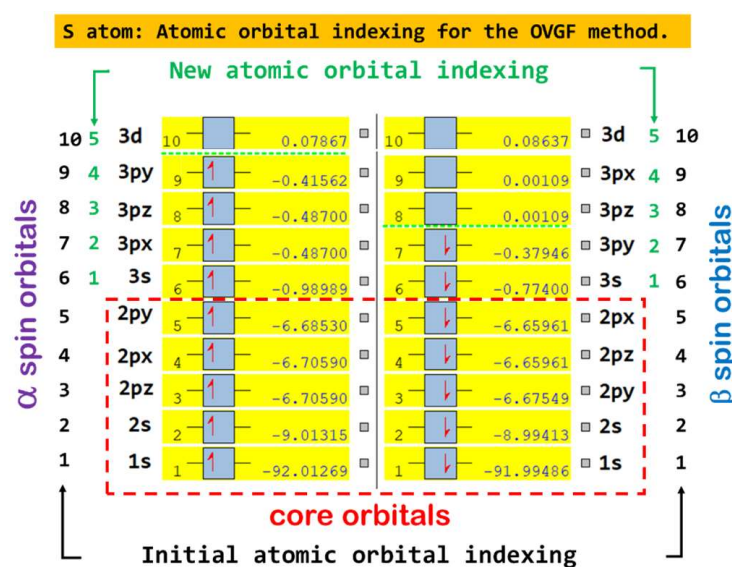


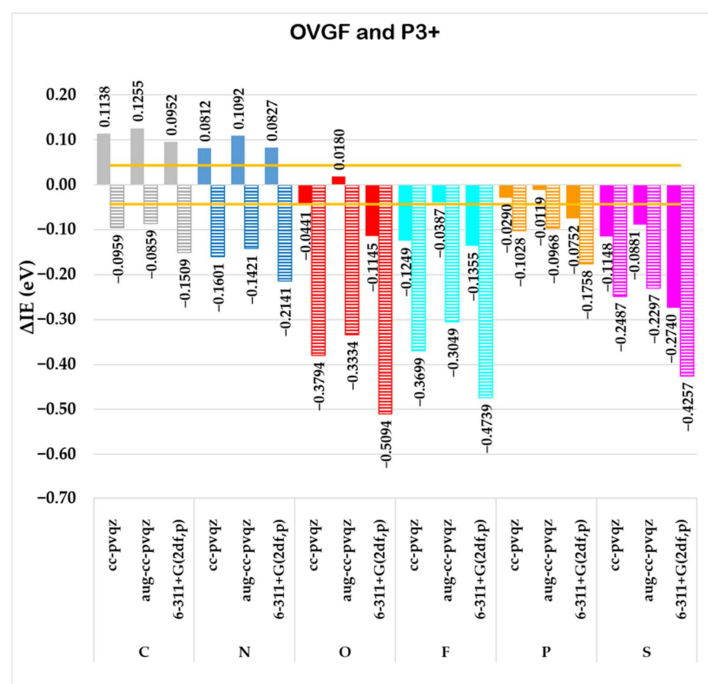
Figure 2. Valence orbitals of the S atom (α type in the left column and β type in the right column) calculated using the OVGf method with the aug-cc-pVQZ basis set.

Table 2 contains the MAE and MSE values averaged over the six atoms for the three basis sets with the OVGf and P3+ methods. Chemical accuracy is not achieved for any combination of basis set and method on average. For OVGf, the smallest MAE is obtained with the aug-cc-pVQZ basis set, followed by cc-pVQZ and then by 6-311+G(2df,p), indicating that the inclusion of diffuse functions improves the description of the ionized state. Higher errors are obtained with the P3+ method, although the same basis set trend is observed as for OVGf.

Table 2. The MAEs and MSEs for C, N, O, F, P, and S atoms, computed for different basis sets for the OVGF and P3+ methods.

Basis Set	MAE OVGF (eV)	MSE OVGF (eV)	MAE P3+ (eV)	MSE P3+ (eV)
cc-pVQZ	0.0847	−0.0197	0.2262	−0.2262
aug-cc-pVQZ	0.0652	0.0190	0.1988	−0.1988
6-311+G(2df,p)	0.1295	−0.0702	0.3250	−0.3250

Figure 3 shows the deviations of the calculated ionization energy with respect to the experimental values for the six atoms for the OVGF and P3+ methods. For the carbon atom, the OVGF overestimates and P3+ underestimates the experimental value. For nitrogen, the OVGF deviations are positive, while the P3+ underestimates the IE. None of the calculated values achieves chemical accuracy for C and N atoms. For oxygen, OVGF/aug-cc-pVQZ yields a deviation of only 0.0180 eV, within chemical accuracy, while the other two basis sets give larger negative deviations. Moreover, the P3+ method strongly underestimates the IE for oxygen, with deviations from the experiment in the range of −0.5094 eV to −0.3334 eV. For fluorine, OVGF/aug-cc-pVQZ achieves chemical accuracy with a deviation of −0.0387 eV, while the P3+ underestimates the IE. For phosphorus, OVGF reaches chemical accuracy with the cc-pVQZ and aug-cc-pVQZ basis sets, yielding deviations of −0.0290 and −0.0119 eV, respectively, while the 6-311+G(2df,p) basis set result is outside the chemical accuracy threshold. The P3+ method underestimates the experimental value for all three basis sets. For sulfur, the OVGF underestimates the IE, while the P3+ method yields large deviations. On average, the 6-311+G(2df,p) basis set yields the largest deviations, while aug-cc-pVQZ gives the smallest, indicating that the inclusion of diffuse functions improves the description of the ionized state. The P3+ method systematically underestimates the experimental ionization energies for all atoms and basis sets, which is reflected by the negative MSE values in Table 2.

**Figure 3.** Deviations (in eV) from the experimental data of the calculated ionization energy of the C, N, O, F, P, and S atoms using the OVGF (solid bars) and P3+ (hatched bars) methods. The horizontal lines define the interval of chemical accuracy.

3.2. Ionization Energies of the H, C, N, O, F, P, and S Atoms Obtained with the Energy-Difference Approach and IP-EOM-CCSD

Since the OVGF and P3+ methods do not achieve chemical accuracy for the considered atoms (Table 1), higher-level coupled-cluster calculations were performed using CCSD(T), CCSDT, and IP-EOM-CCSD methods as implemented in ORCA 6.1.0, combined with the basis set extrapolation to the complete basis set (CBS) limit and scalar relativistic corrections through the DKH2 Hamiltonian. In addition, a series of calculations were carried out with Gaussian 16 using B2PLYP, MP2, CCSD(T), QCISD(T), G3, and CBS-QB3 methods with the default frozen-core approximation, in which only the valence electrons are included in the correlation treatment.

Tables 3–9 summarize the ionization energies of the H, C, N, O, F, P, and S atoms. The upper part of each table reports the results obtained with ORCA 6.1.0 using the CCSD(T), CCSDT, and IP-EOM-CCSD methods with three families of basis sets (aug-cc-pVXZ-DK, aug-cc-pVXZ, and ANO-RCC) together with the corresponding CBS extrapolations. For CCSD(T) and CCSDT, the ionization energies were obtained as total energy differences between the neutral and cationic species, while for the IP-EOM-CCSD method, they were obtained directly from the ionized roots of the neutral reference state. The lower part of the tables shows the results obtained with Gaussian 16 using the frozen-core default approximation and the energy-difference approach for the B2PLYP, MP2, CCSD(T), and QCISD(T) methods combined with the aug-cc-pVQZ basis set, as well as the composite methods G3 and CBS-QB3. All Gaussian calculations employed the default frozen-core approximation. All calculated ionization energies include the atomic spin–orbit corrections described in the Computational Methods section, except for the G3 and CBS-QB3 results, which already contain this contribution. All deviations (Δ IE) are reported relative to the experimental values from NIST Atomic Spectra Database (ver. 5.12) [48]. In addition, the tables provide the spin multiplicities of both the neutral and cationic species. For each atom, the corresponding deviations are also presented graphically in Figures 4–10.

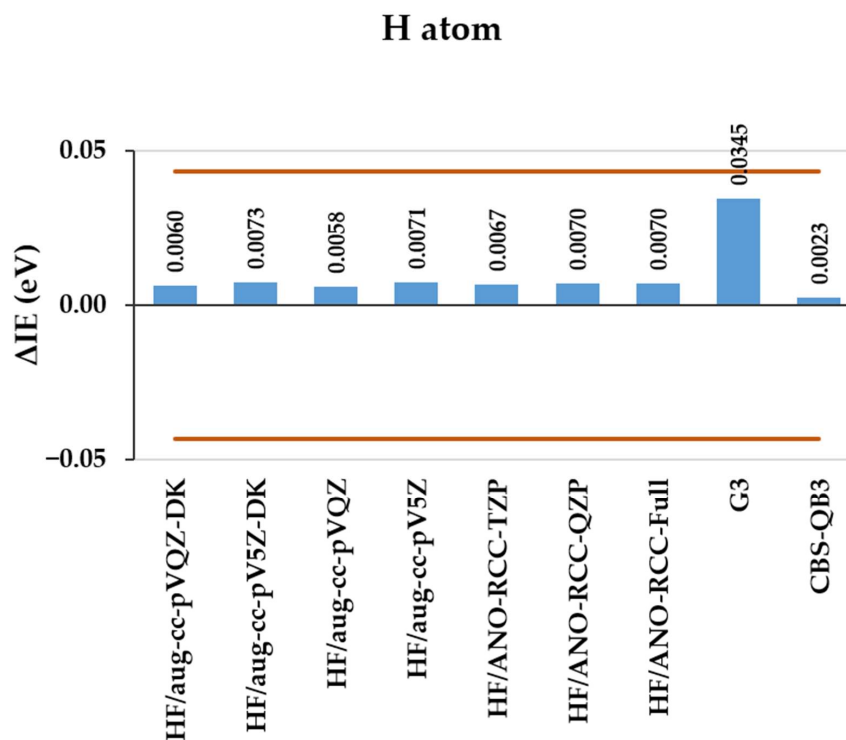


Figure 4. Deviations Δ IE (eV) of the calculated ionization energies of the hydrogen atom from the experimental value. The horizontal lines define the interval of chemical accuracy.

Table 3. Ionization energies of the H atom computed using HF with multiple basis sets and with the composite methods G3 and CBS-QB3.

Atom	Method	Basis Set	Multiplicity (Neutral/Cation)	IE _{calc} (eV)	IE _{exp} (eV) [48]	ΔIE (eV)
H	HF	aug-cc-pVQZ-DK	2/1	13.6045	13.5984	0.0060
		aug-cc-pV5Z-DK	2/1	13.6057	13.5984	0.0073
		aug-cc-pVQZ	2/1	13.6043	13.5984	0.0058
		aug-cc-pV5Z	2/1	13.6056	13.5984	0.0071
		ANO-RCC-TZP	2/1	13.6051	13.5984	0.0067
		ANO-RCC-QZP	2/1	13.6054	13.5984	0.0070
	G3 CBS-QB3	ANO-RCC-Full	2/1	13.6054	13.5984	0.0070
			2/1	13.6330	13.5984	0.0345
			2/1	13.6007	13.5984	0.0023

Table 4. Ionization energies of the C atom computed using CCSD(T), CCSDT, and IP-EOM-CCSD with multiple basis sets and their CBS extrapolation, together with B2PLYP, MP2, CCSD(T), and QCISD(T) obtained with aug-cc-pVQZ, and with the composite G3 and CBS-QB3 methods.

Atom	Method	Basis Set	Multiplicity (Neutral/Cation)	IE _{calc} (eV)	IE _{exp} (eV) [48]	ΔIE (eV)
C	CCSD(T)	aug-cc-pVQZ-DK	3/2	11.2296	11.2603	−0.0307
		aug-cc-pV5Z-DK		11.2460		−0.0143
		SCF(5Z) + corr_CBS(Q,5)		11.2619		0.0016
		aug-cc-pVQZ		11.2333		−0.0270
		aug-cc-pV5Z		11.2497		−0.0106
		SCF(5Z) + corr_CBS(Q,5)		11.2656		0.0053
		ANO-RCC-TZP		11.1946		−0.0657
		ANO-RCC-QZP		11.2147		−0.0456
		ANO-RCC-Full		11.2258		−0.0345
		SCF(QZ) + corr_CBS(T,Q)		11.2321		−0.0282
	CCSDT	aug-cc-pVQZ-DK	3/2	11.2340	11.2603	−0.0263
		aug-cc-pV5Z-DK		11.2500		−0.0103
		SCF(5Z) + corr_CBS(Q,5)		11.2655		0.0052
		aug-cc-pVQZ		11.2378		−0.0225
		aug-cc-pV5Z		11.2537		−0.0066
		SCF(5Z) + corr_CBS(Q,5)		11.2692		0.0089
		ANO-RCC-TZP		11.1998		−0.0605
		ANO-RCC-QZP		11.2197		−0.0406
		ANO-RCC-Full		11.2303		−0.0300
		SCF(QZ) + corr_CBS(T,Q)		11.2368		−0.0235
	IP-EOM-CCSD	aug-cc-pVQZ-DK	3/2	11.2912	11.2603	0.0309
		aug-cc-pV5Z-DK		11.3133		0.0530
		CBS(Q,5)		11.3365		0.0762
		aug-cc-pVQZ		11.2950		0.0347
		aug-cc-pV5Z		11.3171		0.0568
		CBS(Q,5)		11.3403		0.0800
		ANO-RCC-TZP		11.2426		−0.0177
		ANO-RCC-QZP		11.2766		0.0163
		ANO-RCC-Full		11.2956		0.0353
		CBS(T,Q)		11.3013		0.0410
	B2PLYP	aug-cc-pVQZ	3/2	11.3479	11.2603	0.0876
	MP2	aug-cc-pVQZ		11.2785		0.0182
	CCSD(T)	aug-cc-pVQZ		11.1404		−0.1199
	QCISD(T)	aug-cc-pVQZ		11.2056		−0.0547
	G3			11.2114		−0.0489
	CBS-QB3			11.1925		−0.0678

Table 5. Ionization energies of the N atom computed using CCSD(T), CCSDT, and IP-EOM-CCSD with multiple basis sets and their CBS extrapolation, together with B2PLYP, MP2, CCSD(T), and QCISD(T) obtained with aug-cc-pVQZ, and with the composite G3 and CBS-QB3 methods.

Atom	Method	Basis Set	Multiplicity (Neutral/Cation)	IE _{calc} (eV)	IE _{exp} (eV) [48]	ΔIE (eV)
N	CCSD(T)	aug-cc-pVQZ-DK	4/3	14.5079	14.5341	−0.0262
		aug-cc-pV5Z-DK		14.5236		−0.0105
		SCF(5Z) + corr_CBS(Q,5)		14.5396		0.0055
		aug-cc-pVQZ		14.5140		−0.0201
		aug-cc-pV5Z		14.5297		−0.0044
		SCF(5Z) + corr_CBS(Q,5)		14.5457		0.0116
		ANO-RCC-TZP		14.4728		−0.0613
		ANO-RCC-QZP		14.4866		−0.0475
		ANO-RCC-Full		14.5063		−0.0278
		SCF(QZ) + corr_CBS(T,Q)		14.5004		−0.0337

Table 5. Cont.

Atom	Method	Basis Set	Multiplicity (Neutral/Cation)	IE _{calc} (eV)	IE _{exp} (eV) [48]	ΔIE (eV)
N	CCSDT	aug-cc-pVQZ-DK	4/3	14.5082	14.5341	−0.0259
		aug-cc-pV5Z-DK		14.5236		−0.0105
		SCF(5Z) + corr_CBS(Q,5)		14.5392		0.0051
		aug-cc-pVQZ		14.5143		−0.0198
		aug-cc-pV5Z		14.5297		−0.0044
		SCF(5Z) + corr_CBS(Q,5)		14.5453		0.0112
		ANO-RCC-TZP		14.4735		−0.0606
		ANO-RCC-QZP		14.4872		−0.0469
		ANO-RCC-Full		14.5066		−0.0275
		SCF(QZ) + corr_CBS(T,Q)		14.5009		−0.0332
	IP-EOM-CCSD	aug-cc-pVQZ-DK		14.5331		−0.0010
		aug-cc-pV5Z-DK		14.5569		0.0228
		CBS(Q,5)		14.5820		0.0479
		aug-cc-pVQZ		14.5393		0.0052
		aug-cc-pV5Z		14.5631		0.0290
		CBS(Q,5)		14.5880		0.0539
		ANO-RCC-TZP		14.4753		−0.0588
		ANO-RCC-QZP		14.5123		−0.0218
		ANO-RCC-Full		14.5377		0.0036
		CBS(T,Q)		14.5392		0.0051
	B2PLYP	aug-cc-pVQZ		14.5061		−0.0280
	MP2	aug-cc-pVQZ		14.5916		0.0575
	CCSD(T)	aug-cc-pVQZ		14.4891		−0.0450
	QCISD(T)	aug-cc-pVQZ		14.4891		−0.0450
	G3			14.5068		−0.0273
	CBS-QB3			14.4927		−0.0415

Table 6. Ionization energies of the O atom computed using CCSD(T), CCSDT, and IP-EOM-CCSD with multiple basis sets and their CBS extrapolation, together with B2PLYP, MP2, CCSD(T), and QCISD(T) obtained with aug-cc-pVQZ, and with the composite G3 and CBS-QB3 methods.

Atom	Method	Basis Set	Multiplicity (Neutral/Cation)	IE _{calc} (eV)	IE _{exp} (eV) [48]	ΔIE (eV)
O	CCSD(T)	aug-cc-pVQZ-DK	3/4	13.5301	13.6181	−0.0880
		aug-cc-pV5Z-DK		13.5717		−0.0464
		SCF(5Z) + corr_CBS(Q,5)		13.6163		−0.0018
		aug-cc-pVQZ		13.5391		−0.0790
		aug-cc-pV5Z		13.5807		−0.0374
		SCF(5Z) + corr_CBS(Q,5)		13.6252		0.0071
		ANO-RCC-TZP		13.3927		−0.2254
		ANO-RCC-QZP		13.4537		−0.1644
		ANO-RCC-Full		13.5246		−0.0935
		SCF(QZ) + corr_CBS(T,Q)		13.5093		−0.1088
	CCSDT	aug-cc-pVQZ-DK		13.5335		−0.0846
		aug-cc-pV5Z-DK		13.5748		−0.0433
		SCF(5Z) + corr_CBS(Q,5)		13.6191		0.0010
		aug-cc-pVQZ		13.5425		−0.0756
		aug-cc-pV5Z		13.5838		−0.0343
		SCF(5Z) + corr_CBS(Q,5)		13.6280		0.0099
		ANO-RCC-TZP		13.3963		−0.2218
		ANO-RCC-QZP		13.4574		−0.1607
		ANO-RCC-Full		13.5280		−0.0901
		SCF(QZ) + corr_CBS(T,Q)		13.5131		−0.1050
	IP-EOM-CCSD	aug-cc-pVQZ-DK		13.5547		−0.0634
		aug-cc-pV5Z-DK		13.6051		−0.0130
		CBS(Q,5)		13.6580		0.0399
		aug-cc-pVQZ		13.5637		−0.0544
		aug-cc-pV5Z		13.6140		−0.0041
		CBS(Q,5)		13.6668		0.0487
		ANO-RCC-TZP		13.3840		−0.2341
		ANO-RCC-QZP		13.4703		−0.1478
		ANO-RCC-Full		13.5551		−0.0630
		CBS(T,Q)		13.5333		−0.0848
	B2PLYP	aug-cc-pVQZ		13.8243		0.2062
	MP2	aug-cc-pVQZ		13.4708		−0.1473
	CCSD(T)	aug-cc-pVQZ		13.5234		−0.0947
	QCISD(T)	aug-cc-pVQZ		13.5246		−0.0935
	G3			13.5478		−0.0702
	CBS-QB3			13.5869		−0.0311

Table 7. Ionization energies of the F atom computed using CCSD(T), CCSDT, and IP-EOM-CCSD with multiple basis sets and their CBS extrapolation, together with B2PLYP, MP2, CCSD(T), and QCISD(T) obtained with aug-cc-pVQZ, and with the composite G3 and CBS-QB3 methods.

Atom	Method	Basis Set	Multiplicity (Neutral/Cation)	IE _{calc} (eV)	IE _{exp} (eV) [48]	ΔIE (eV)
F	CCSD(T)	aug-cc-pVQZ-DK	2/3	17.3447	17.4228	−0.0781
		aug-cc-pV5Z-DK		17.3822		−0.0406
		SCF(5Z) + corr_CBS(Q,5)		17.4242		0.0014
		aug-cc-pVQZ		17.3575		−0.0653
		aug-cc-pV5Z		17.3949		−0.0279
		SCF(5Z) + corr_CBS(Q,5)		17.4369		0.0141
		ANO-RCC-TZP		17.1938		−0.2290
		ANO-RCC-QZP		17.2597		−0.1631
		ANO-RCC-Full		17.3402		−0.0826
		SCF(QZ) + corr_CBS(T,Q)		17.3210		−0.1018
	CCSDT	aug-cc-pVQZ-DK	2/3	17.3447	17.4228	−0.0781
		aug-cc-pV5Z-DK		17.3818		−0.0410
		SCF(5Z) + corr_CBS(Q,5)		17.4234		0.0006
		aug-cc-pVQZ		17.3575		−0.0653
		aug-cc-pV5Z		17.3946		−0.0282
		SCF(5Z) + corr_CBS(Q,5)		17.4362		0.0134
		ANO-RCC-TZP		17.1949		−0.2279
		ANO-RCC-QZP		17.2601		−0.1627
		ANO-RCC-Full		17.3401		−0.0827
		SCF(QZ) + corr_CBS(T,Q)		17.3211		−0.1017
	IP-EOM-CCSD	aug-cc-pVQZ-DK	2/3	17.3170	17.4228	−0.1058
		aug-cc-pV5Z-DK		17.3690		−0.0538
		CBS(Q,5)		17.4235		0.0007
		aug-cc-pVQZ		17.3298		−0.0930
		aug-cc-pV5Z		17.3817		−0.0411
		CBS(Q,5)		17.4361		0.0133
		ANO-RCC-TZP		17.1313		−0.2915
		ANO-RCC-QZP		17.2218		−0.2010
		ANO-RCC-Full		17.3200		−0.1028
		CBS(T,Q)		17.2879		−0.1349
	B2PLYP	aug-cc-pVQZ	2/3	18.8210	17.4228	1.3982
	MP2	aug-cc-pVQZ		17.3917		−0.0311
	CCSD(T)	aug-cc-pVQZ		17.3423		−0.0805
	QCISD(T)	aug-cc-pVQZ		17.3445		−0.0783
	G3	aug-cc-pVQZ		17.3884		−0.0344
	CBS-QB3	aug-cc-pVQZ		17.4741		0.0513

Table 8. Ionization energies of the P atom computed using CCSD(T), CCSDT, and IP-EOM-CCSD with multiple basis sets and their CBS extrapolation, together with B2PLYP, MP2, CCSD(T), and QCISD(T) obtained with aug-cc-pVQZ, and with the composite G3 and CBS-QB3 methods.

Atom	Method	BASIS SET	Multiplicity (Neutral/Cation)	IE _{calc} (eV)	IE _{exp} (eV) [48]	ΔIE (eV)
P	CCSD(T)	aug-cc-pVQZ-DK	4/3	10.4405	10.4867	−0.0462
		aug-cc-pV5Z-DK		10.4612		−0.0255
		SCF(5Z) + corr_CBS(Q,5)		10.4851		−0.0016
		aug-cc-pVQZ		10.4525		−0.0342
		aug-cc-pV5Z		10.4733		−0.0134
		SCF(5Z) + corr_CBS(Q,5)		10.4974		0.0107
		ANO-RCC-TZP		10.4106		−0.0761
		ANO-RCC-QZP		10.4203		−0.0664
		ANO-RCC-Full		10.4499		−0.0368
		SCF(QZ) + corr_CBS(T,Q)		10.4281		−0.0586
	CCSDT	aug-cc-pVQZ-DK	4/3	10.4429	10.4867	−0.0438
		aug-cc-pV5Z-DK		10.4625		−0.0242
		SCF(5Z) + corr_CBS(Q,5)		10.4854		−0.0013
		aug-cc-pVQZ		10.4548		−0.0319
		aug-cc-pV5Z		10.4746		−0.0121
		SCF(5Z) + corr_CBS(Q,5)		10.4977		0.0110
		ANO-RCC-TZP		10.4144		−0.0723
		ANO-RCC-QZP		10.4233		−0.0634
		ANO-RCC-Full		10.4518		−0.0349
		SCF(QZ) + corr_CBS(T,Q)		10.4304		−0.0563

Table 8. Cont.

Atom	Method	BASIS SET	Multiplicity (Neutral/Cation)	IE _{calc} (eV)	IE _{exp} (eV) [48]	ΔIE (eV)
P	IP-EOM-CCSD	aug-cc-pVQZ-DK	4/3	10.4668	10.4867	−0.0199
		aug-cc-pV5Z-DK		10.5038		0.0171
		CBS(Q,5)		10.5426		0.0559
		aug-cc-pVQZ		10.4786		−0.0081
		aug-cc-pV5Z		10.5158		0.0291
		CBS(Q,5)		10.5548		0.0681
		ANO-RCC-TZP		10.4317		−0.0550
		ANO-RCC-QZP		10.4474		−0.0393
		ANO-RCC-Full		10.4946		0.0079
		CBS(T,Q)		10.4589		−0.0278
	B2PLYP	aug-cc-pVQZ		10.3031		−0.1836
	MP2	aug-cc-pVQZ		10.4505		−0.0362
	CCSD(T)	aug-cc-pVQZ		10.4615		−0.0252
	QCISD(T)	aug-cc-pVQZ		10.4601		−0.0266
	G3			10.4637		−0.0230
	CBS-QB3			10.4472		−0.0394

Table 9. Ionization energies of the S atom computed using CCSD(T), CCSDT, and IP-EOM-CCSD with multiple basis sets and their CBS extrapolation, together with B2PLYP, MP2, CCSD(T), and QCISD(T) obtained with aug-cc-pVQZ, and with the composite G3 and CBS-QB3 methods.

Atom	Method	Basis Set	Multiplicity (Neutral/Cation)	IE _{calc} (eV)	IE _{exp} (eV) [48]	ΔIE (eV)
S	CCSD(T)	aug-cc-pVQZ-DK	3/4	10.2657	10.3600	−0.0943
		aug-cc-pV5Z-DK		10.3085		−0.0515
		SCF(5Z) + corr_CBS(Q,5)		10.3540		−0.0060
		aug-cc-pVQZ		10.2797		−0.0803
		aug-cc-pV5Z		10.3227		−0.0373
		SCF(5Z) + corr_CBS(Q,5)		10.3684		0.0084
		ANO-RCC-TZP		10.1356		−0.2244
		ANO-RCC-QZP		10.1731		−0.1869
		ANO-RCC-Full		10.2785		−0.0815
		SCF(QZ) + corr_CBS(T,Q)		10.1989		−0.1611
	CCSDT	aug-cc-pVQZ-DK		10.2695		−0.0905
		aug-cc-pV5Z-DK		10.3122		−0.0478
		SCF(5Z) + corr_CBS(Q,5)		10.3575		−0.0025
		aug-cc-pVQZ		10.2835		−0.0765
		aug-cc-pV5Z		10.3264		−0.0336
		SCF(5Z) + corr_CBS(Q,5)		10.3719		0.0119
		ANO-RCC-TZP		10.1383		−0.2217
		ANO-RCC-QZP		10.1760		−0.1840
	IP-EOM-CCSD	ANO-RCC-Full		10.2824		−0.0776
		SCF(QZ) + corr_CBS(T,Q)		10.2021		−0.1579
		aug-cc-pVQZ-DK		10.3428		−0.0172
		aug-cc-pV5Z-DK		10.4012		0.0412
		CBS(Q,5)		10.4625		0.1025
		aug-cc-pVQZ		10.3573		−0.0027
		aug-cc-pV5Z		10.4158		0.0558
		CBS(Q,5)		10.4773		0.1173
		ANO-RCC-TZP		10.2108		−0.1492
		ANO-RCC-QZP		10.2551		−0.1049
	B2PLYP	ANO-RCC-Full		10.3736		0.0136
		CBS(T,Q)		10.2874		−0.0726
		aug-cc-pVQZ		10.3796		0.0196
		aug-cc-pVQZ		10.1639		−0.1961
		CCSD(T)		10.2779		−0.0821
		QCISD(T)		10.2793		−0.0807
	G3			10.2691		−0.0909
	CBS-QB3			10.2444		−0.1156

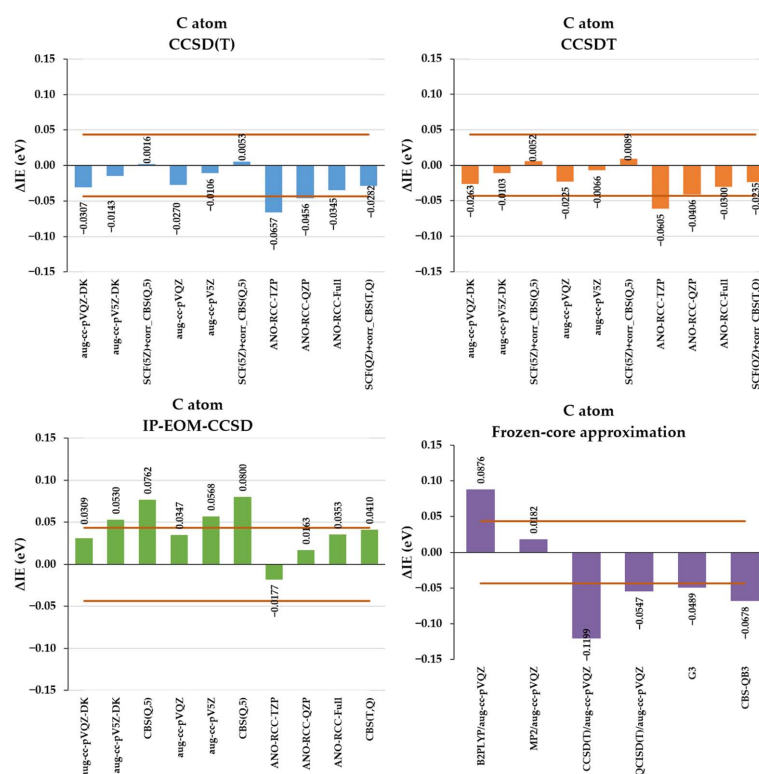


Figure 5. Deviations ΔIE (eV) of the calculated ionization energies of the carbon atom from the experimental value for CCSD(T), CCSDT, IP-EOM-CCSD, and the methods employing frozen-core approximation. The horizontal lines define the interval of chemical accuracy.

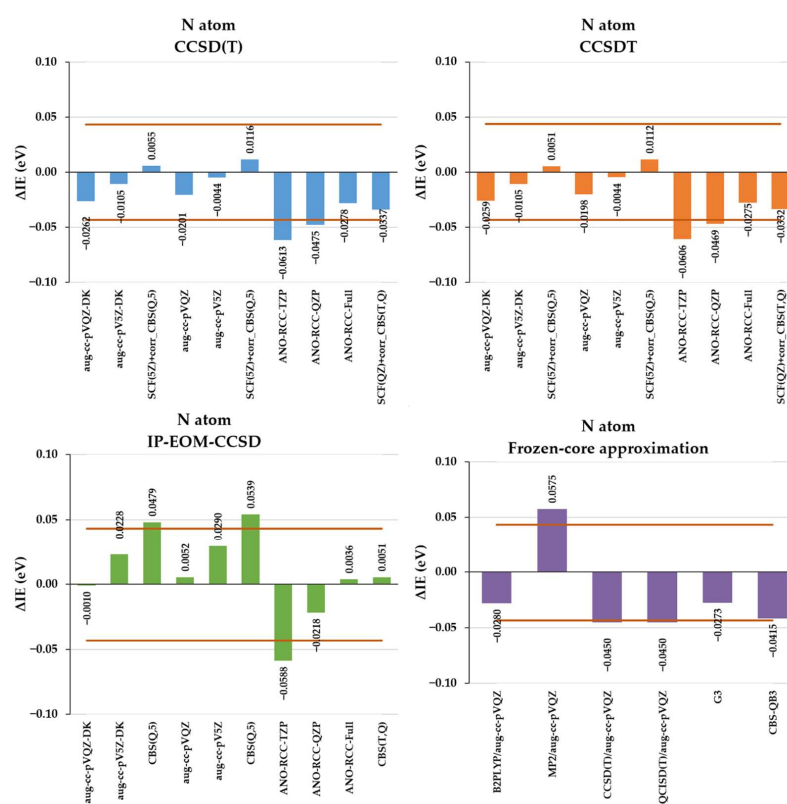


Figure 6. Deviations ΔIE (eV) of the calculated ionization energies of the nitrogen atom from the experimental value for CCSD(T), CCSDT, IP-EOM-CCSD, and the methods employing frozen-core approximation. The horizontal lines define the interval of chemical accuracy.

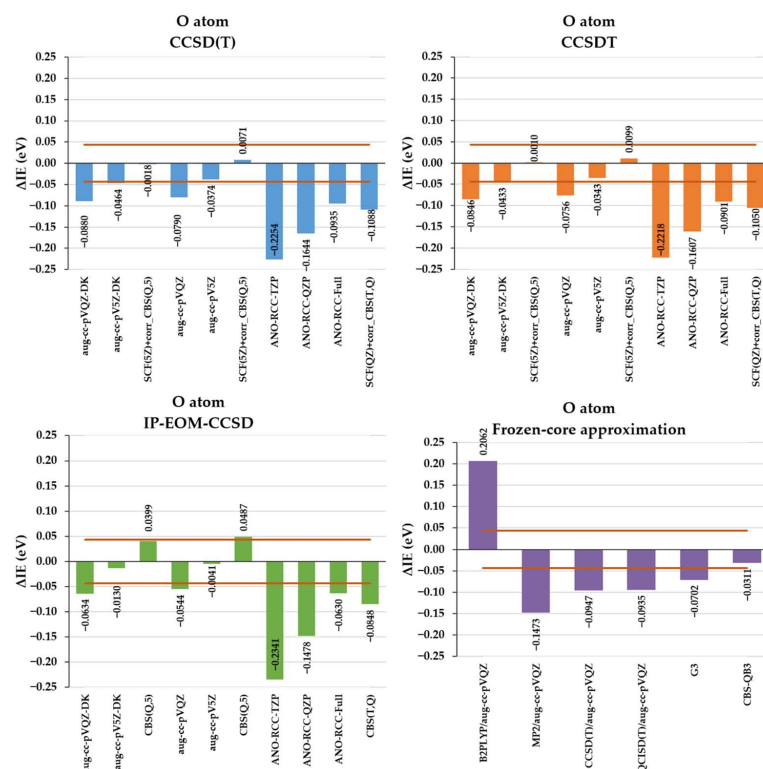


Figure 7. Deviations ΔIE (eV) of the calculated ionization energies of the oxygen atom from the experimental value for CCSD(T), CCSDT, IP-EOM-CCSD, and the methods employing frozen-core approximation. The horizontal lines define the interval of chemical accuracy.

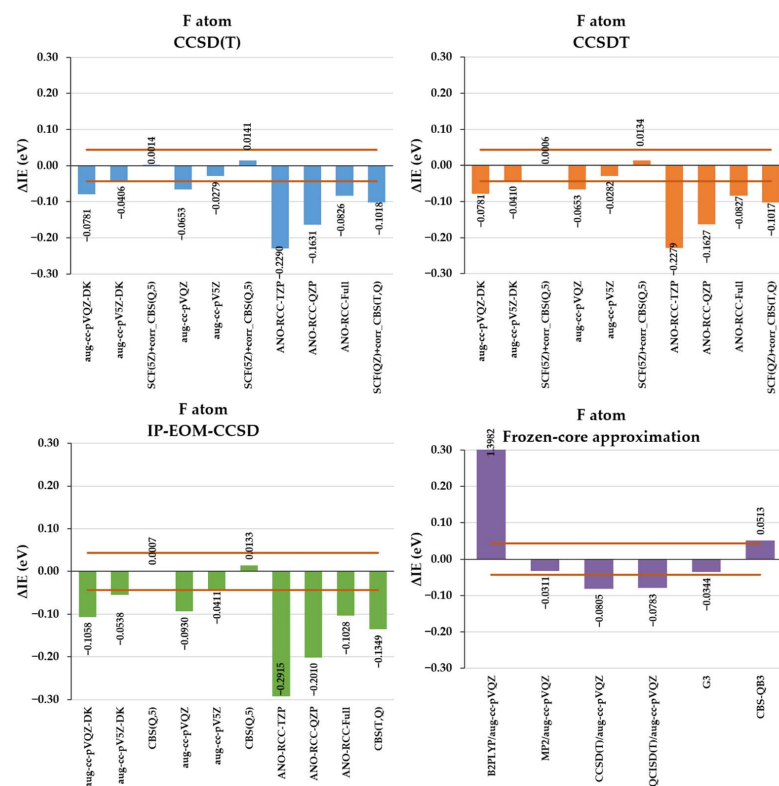


Figure 8. Deviations ΔIE (eV) of the calculated ionization energies of the fluorine atom from the experimental value for CCSD(T), CCSDT, IP-EOM-CCSD, and the methods employing frozen-core approximation. The horizontal lines define the interval of chemical accuracy.

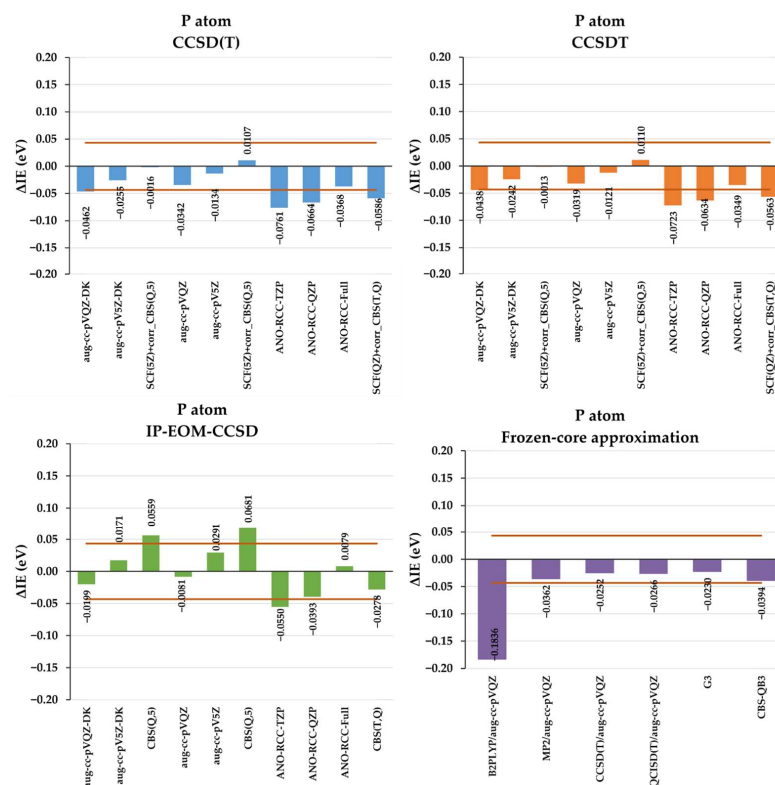


Figure 9. Deviations ΔIE (eV) of the calculated ionization energies of the phosphorus atom from the experimental value for CCSD(T), CCSDT, IP-EOM-CCSD, and the methods employing frozen-core approximation. The horizontal lines define the interval of chemical accuracy.

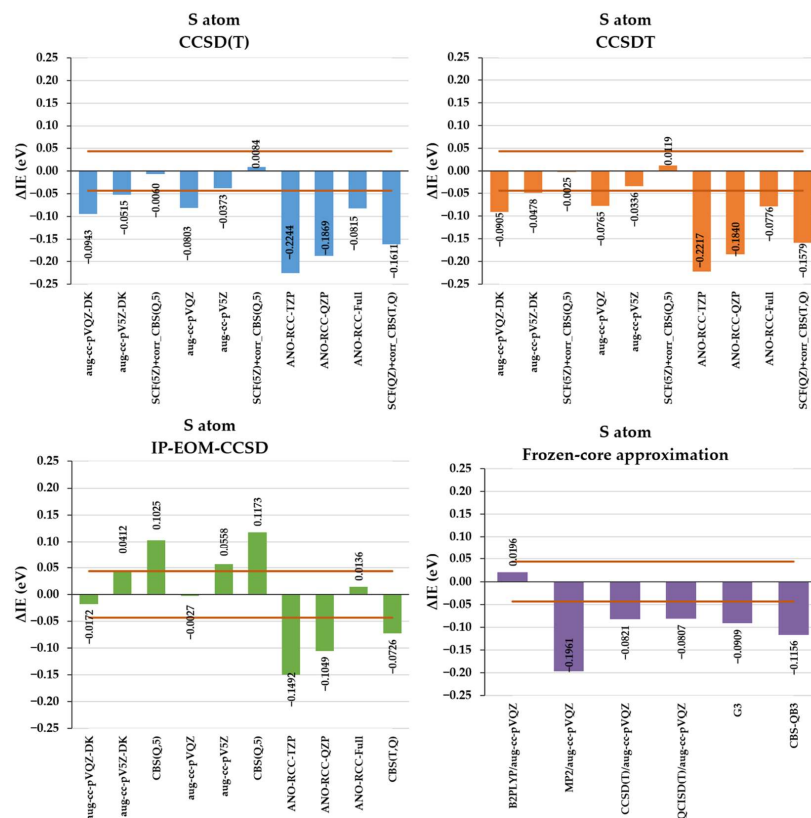


Figure 10. Deviations ΔIE (eV) of the calculated ionization energies of the sulfur atom from the experimental value for CCSD(T), CCSDT, IP-EOM-CCSD, and the methods employing frozen-core approximation. The horizontal lines define the interval of chemical accuracy.

For the **hydrogen atom** (Table 3), which is a single-electron system, there is no electron correlation, and the ionization energy corresponds to the Hartree–Fock (HF) value. HF calculations were performed with three families of basis sets: the aug-cc-pVXZ ($X = Q, 5$), the relativistic aug-cc-pVXZ-DK ($X = Q, 5$) including the DKH2 Hamiltonian, and the ANO-RCC basis sets at the TZP, QZP, and Full contraction levels. All computed IE values are within the range of 13.6043–13.6057 eV, with deviations ranging from 0.0058 to 0.0073 eV relative to the experimental value of 13.5984 eV, which are clearly within chemical accuracy. The effect of scalar relativistic corrections (DKH2) is minimal for H, corresponding to only 0.0001 eV, as seen from the comparison between the values obtained with aug-cc-pV5Z-DK and aug-cc-pV5Z. The ANO-RCC basis sets already converge at the TZP contraction level (13.6051 eV), with QZP and Full giving identical values (13.6054 eV). Moreover, the G3 and CBS-QB3 yield 13.6330 eV ($\Delta IE = 0.0345$ eV) and 13.6007 eV ($\Delta IE = 0.0023$ eV), respectively, with CBS-QB3 providing the closest agreement with the experiment among all methods considered for this atom.

These results are also presented in Figure 4, which shows that IE values for the hydrogen atom are well within the chemical accuracy interval, with only minor differences between the basis sets.

In the case of the **carbon atom** (Table 4), the CCSD(T)/aug-cc-pVXZ-DK ionization energy values converge from 11.2296 eV (QZ, $\Delta IE = -0.0307$ eV) to 11.2460 eV (5Z, $\Delta IE = -0.0143$ eV), while the CBS extrapolation yields 11.2619 eV ($\Delta IE = 0.0016$ eV), in excellent agreement with the experiment. CCSDT yields slightly smaller deviations than CCSD(T) (-0.0263 with aug-cc-pVQZ-DK and -0.0103 eV with aug-cc-pV5Z-DK), as expected from the iterative treatment of triple excitations. With the CBS extrapolation, CCSDT produces a CBS value of 11.2655 eV ($\Delta IE = 0.0052$ eV), with a difference of only 0.0036 eV above the CCSD(T)/CBS value. Both protocols remain well within chemical accuracy, indicating that the perturbative triples correction in CCSD(T) is enough for an accurate description of the carbon ionization energy. For IP-EOM-CCSD, the first ionization is attributed to the α -electron removal. By contrast, the IP-EOM-CCSD method already overestimates the IE at the QZ level by 0.0309 eV, and the deviation increases further with the basis set, reaching 0.0530 eV at 5Z and 0.0762 eV at the CBS limit. This trend is different from that observed for CCSD(T) and CCSDT. It can be explained by the absence of explicit triple excitations in IP-EOM-CCSD. With the increase in the basis set size, the basis set incompleteness error is reduced, and the missing contribution from triple excitations becomes more visible.

The aug-cc-pVXZ results follow a similar pattern, with the CCSD(T) and CCSDT CBS values at 11.2656 eV ($\Delta IE = 0.0053$ eV) and 11.2692 eV ($\Delta IE = 0.0089$ eV), respectively, both within chemical accuracy. The non-relativistic IP-EOM-CCSD CBS value of 11.3403 eV ($\Delta IE = 0.0800$ eV) shows the same overestimation pattern. The DKH2 contribution is approximately -0.0037 eV across all methods and basis sets.

With ANO-RCC basis sets, the CCSD(T) values increase from 11.1946 eV (TZP) to 11.2147 eV (QZP) and 11.2258 eV (Full), the last value being within chemical accuracy (Full, $\Delta IE = -0.0345$ eV). The CBS(T,Q) extrapolation yields 11.2321 eV ($\Delta IE = -0.0282$ eV), also within chemical accuracy but further from experiment than the aug-cc CBS results. The CCSDT CBS(T,Q) extrapolation value is 11.2368 eV ($\Delta IE = -0.0235$ eV), while IP-EOM-CCSD CBS(T,Q) reaches 11.3013 eV ($\Delta IE = 0.0410$ eV) at the chemical accuracy limit.

Among the Gaussian 16 results with the aug-cc-pVQZ basis set, B2PLYP overestimates the IE by 0.0876 eV, while MP2 gives a deviation of 0.0182 eV. CCSD(T) and QCISD(T) yield deviations of -0.1199 eV and -0.0547 eV, respectively. The results of the composite methods G3 and CBS-QB3 are 11.2114 eV ($\Delta IE = -0.0489$ eV) and 11.1925 eV ($\Delta IE = -0.0678$ eV), respectively.

A graphical summary of the deviations from the experimental value corresponding to the C atom is depicted in Figure 5. The four panels clearly show the good agreement with the experiment obtained for CCSD(T) and CCSDT, particularly with the CBS extrapolation, the systematic overestimation by the IP-EOM-CCSD method with the aug-cc basis sets, and the large negative deviations observed with the frozen-core methods.

For the **nitrogen atom** (Table 5), the CCSD(T)/aug-cc-pVXZ-DK ionization energy values converge from 14.5079 eV (QZ, $\Delta IE = -0.0262$ eV) to 14.5236 eV (5Z, $\Delta IE = -0.0105$ eV), and the CBS extrapolation yields 14.5396 eV ($\Delta IE = 0.0055$ eV), very close to the experimental value of 14.5341 eV. CCSDT yields identical results, with QZ, 5Z, and CBS-DK deviations of -0.0259 , -0.0105 , and 0.0051 eV, respectively. This indicates that, for the nitrogen atom, the iterative treatment of triple excitations does not lead to a significant change compared with the perturbative treatment used in CCSD(T). For IP-EOM-CCSD, the first ionization corresponds to the lowest α electron removal root. The aug-cc-pVQZ-DK value is in nearly perfect agreement with experiment ($\Delta IE = -0.0010$ eV), but the deviation increases systematically with the basis set, reaching 0.0228 eV at 5Z and 0.0479 eV at the CBS limit, outside chemical accuracy, following the same trend as for the carbon atom.

The aug-cc-pVXZ calculations follow the same pattern, with CCSD(T) CBS at 14.5457 eV ($\Delta IE = 0.0116$ eV) and CCSDT CBS at 14.5453 eV ($\Delta IE = 0.0112$ eV), both within chemical accuracy. The IP-EOM-CCSD CBS value of 14.5880 eV ($\Delta IE = 0.0539$ eV) remains outside the threshold. The DKH2 contribution is -0.0061 eV, larger than for carbon (-0.0037 eV), consistent with the higher nuclear charge.

With the ANO-RCC basis sets, the CCSD(T) values increase from 14.4728 eV (TZP, $\Delta IE = -0.0613$ eV) to 14.4866 eV (QZP, $\Delta IE = -0.0475$ eV) and 14.5063 eV (Full, $\Delta IE = -0.0278$ eV), with only the Full value being within chemical accuracy. The CBS(T,Q) extrapolation yields 14.5004 eV ($\Delta IE = -0.0337$ eV), also within chemical accuracy. CCSDT and IP-EOM-CCSD follow the same pattern, with ANO-RCC-Full values of 14.5066 eV ($\Delta IE = -0.0275$ eV) and 14.5377 eV ($\Delta IE = 0.0036$ eV), respectively.

Furthermore, B2PLYP exhibits a deviation of -0.0280 eV, lower than 0.0434 eV, while MP2 overestimates the value of IE by 0.0575 eV. CCSD(T) and QCISD(T) yield identical deviations of -0.0450 eV, slightly outside chemical accuracy. The G3 and CBS-QB3 exhibit deviations of -0.0273 eV and -0.0415 eV, respectively, both within chemical accuracy.

Figure 6 presents the comparison of the ΔIE values for the nitrogen atom. The CCSD(T) and CCSDT results obtained with the aug-cc-pVXZ and aug-cc-pVXZ-DK basis sets are close to zero, confirming the fast basis set convergence observed for this atom, while the IP-EOM-CCSD panel shows the progressive overestimation with increasing the basis set size.

In the case of **the oxygen atom** (Table 6), the CCSD(T) method with the aug-cc-pVXZ-DK basis sets yields IE values that converge systematically from 13.5301 eV at the QZ level ($\Delta IE = -0.0880$ eV) to 13.5717 eV at the 5Z level ($\Delta IE = -0.0464$ eV). The CBS value obtained with the SCF(5Z) + CBS(Q,5)-extrapolated correlation energy scheme is 13.6163 eV ($\Delta IE = -0.0018$ eV), in excellent agreement with the experiment. The CCSDT results follow the same convergence pattern, with the CBS value of 13.6191 eV ($\Delta IE = 0.0010$ eV), confirming that the perturbative triples correction in CCSD(T) is enough for an accurate description of the ionization energy, since the difference between the two methods at the CBS limit is only 0.0028 eV. For the IP-EOM-CCSD, the first ionization corresponds to the lowest β electron removal. The CBS value of 13.6580 eV ($\Delta IE = 0.0399$ eV) remains within chemical accuracy, although the positive deviation indicates a slight overestimation of the experimental value. The best agreement for this method is obtained at the 5Z level ($\Delta IE = -0.0130$ eV).

The non-relativistic calculations with the aug-cc-pVXZ basis sets show a similar convergence but with higher ionization energy values. For CCSD(T), the CBS value is 13.6252 eV

($\Delta IE = 0.0071$ eV), within chemical accuracy. For CCSDT, the CBS value of 13.6280 eV ($\Delta IE = 0.0099$ eV) is also within chemical accuracy. The IP-EOM-CCSD CBS value of 13.6668 eV ($\Delta IE = 0.0487$ eV) follows the same trend but slightly exceeds the chemical accuracy threshold. The contribution of DKH2 scalar relativistic correction to the IE of oxygen is constant, with a value of approximately -0.0090 eV across all methods and basis sets.

The ANO-RCC basis sets show a significantly slower convergence. For CCSD(T), the ionization energy increases from 13.3927 eV (TZP, $\Delta IE = -0.2254$ eV) to 13.4537 eV (QZP, $\Delta IE = -0.1644$ eV) and 13.5246 eV (Full, $\Delta IE = -0.0935$ eV), although none of them achieves chemical accuracy. The CBS(T,Q) extrapolation yields 13.5093 eV ($\Delta IE = -0.1088$ eV), which is less accurate than the Full contraction result. This behavior can be explained by the absence of diffuse functions in the ANO-RCC family. The same trend is observed for CCSDT and IP-EOM-CCSD, with ANO-RCC-Full values of 13.5280 eV ($\Delta IE = -0.0901$ eV) and 13.5551 eV ($\Delta IE = -0.0630$ eV), respectively.

For the results obtained with Gaussian 16 using the aug-cc-pVQZ basis set, B2PLYP overestimates the IE by 0.2062 eV, while MP2 underestimates it by 0.1473 eV. CCSD(T) and QCISD(T) yield similar deviations of -0.0947 eV and -0.0935 eV, respectively. None of these methods achieves chemical accuracy. Moreover, the G3 and CBS-QB3 methods yield values of 13.5478 eV ($\Delta IE = -0.0702$ eV) and 13.5869 eV ($\Delta IE = -0.0311$ eV), respectively. The CBS-QB3 result is within chemical accuracy, whereas the G3 result remains outside this threshold.

The corresponding deviations are illustrated in Figure 7, where the convergence from negative ΔIE values at the QZ and 5Z levels toward the experimental value at the CBS limit is visible for both CCSD(T) and CCSDT. The large underestimation with the ANO-RCC basis sets is also visible.

For the **fluorine atom** (Table 7), the CCSD(T)/aug-cc-pVXZ-DK converges from 17.3447 eV (QZ, $\Delta IE = -0.0781$ eV) to 17.3822 eV (5Z, $\Delta IE = -0.0406$ eV), and the CBS value of 17.4242 eV ($\Delta IE = 0.0014$ eV) achieves chemical accuracy. CCSDT yields essentially identical IE values at the QZ level (17.3447 eV, $\Delta IE = -0.0781$ eV) and slightly smaller deviations at 5Z (-0.0410 eV) and CBS (0.0006 eV). This shows that, for fluorine, the iterative treatment of triple excitations does not significantly change the results compared with CCSD(T). For IP-EOM-CCSD, the first ionization is attributed to the lowest β electron removal root. Both QZ ($\Delta IE = -0.1058$ eV) and 5Z ($\Delta IE = -0.0538$ eV) underestimate the experimental value, and the CBS extrapolation yields 17.4235 eV ($\Delta IE = 0.0007$ eV), which is within chemical accuracy.

The aug-cc-pVXZ results have higher ionization energy values. The CCSD(T) CBS is 17.4369 eV ($\Delta IE = 0.0141$ eV), and the CCSDT CBS is 17.4362 eV ($\Delta IE = 0.0134$ eV), both within chemical accuracy. The IP-EOM-CCSD CBS value of 17.4361 eV ($\Delta IE = 0.0133$ eV) also remains within the threshold. The DKH2 contribution is -0.0127 eV, the largest among the period 2 atoms, consistent with fluorine having the highest nuclear charge in this group.

The ANO-RCC basis sets also show a slow convergence for this atom. CCSD(T) values range from 17.1938 eV (TZP, $\Delta IE = -0.2290$ eV) to 17.2597 eV (QZP, $\Delta IE = -0.1631$ eV) and 17.3402 eV (Full, $\Delta IE = -0.0826$ eV), with none achieving chemical accuracy. The CBS(T,Q) extrapolation yields 17.3210 eV ($\Delta IE = -0.1018$ eV), again showing a larger deviation than the Full result. Moreover, the CCSDT values follow the same trend, underestimating the ionization energy by 0.2279 eV (TZP), 0.1627 eV (QZP), 0.0827 eV (Full), and 0.1017 eV (CBS(T,Q)). For IP-EOM-CCSD, the ANO-RCC-Full and CBS(T,Q) deviations of -0.1028 eV and -0.1349 eV are both far from chemical accuracy.

Furthermore, B2PLYP strongly overestimates IE by 1.3982 eV, the largest error observed for any method across all atoms studied. MP2 gives a deviation of -0.0311 eV, within chemical accuracy. CCSD(T) and QCISD(T) yield similar deviations of -0.0805 eV and

−0.0783 eV, respectively. G3 and CBS-QB3 methods exhibit deviations of −0.0344 eV and 0.0513 eV, respectively, only the G3 result being within chemical accuracy.

As shown in Figure 8, for the fluorine atom, the CCSD(T), CCSDT, and IP-EOM-CCSD values improve with the basis set, and the CBS extrapolations achieve chemical accuracy. The anomalous B2PLYP overestimation is clearly visible in the frozen-core panel. For clarity, the vertical axis was limited to 0.3 eV, even though the B2PLYP deviation is significantly higher, at 1.3982 eV.

In the case of the **phosphorus atom** (Table 8), the CCSD(T)/aug-cc-pVXZ-DK ionization energy converges from 10.4405 eV at the QZ level ($\Delta\text{IE} = -0.0462$ eV) to 10.4612 eV at the 5Z level ($\Delta\text{IE} = -0.0255$ eV), and the CBS extrapolation yields 10.4851 eV ($\Delta\text{IE} = -0.0016$ eV), in excellent agreement with the experimental value of 10.4867 eV. The CCSDT method gives slightly smaller deviations at all levels, −0.0438, −0.0242, and −0.0013 eV for QZ, 5Z, and CBS, respectively. This shows that the iterative treatment of triple excitations changes the results only slightly compared with CCSD(T). For IP-EOM-CCSD, the first ionization corresponds to the lowest root associated with the α electron removal. The aug-cc-pVQZ-DK value underestimates the experimental IE ($\Delta\text{IE} = -0.0199$ eV), while at the 5Z and CBS levels the deviation becomes positive, with values of 0.0171 eV (5Z) and 0.0559 eV (CBS), the latter exceeding the chemical accuracy threshold.

The aug-cc-pVXZ calculations yield systematically higher values. The CCSD(T) CBS of 10.4974 eV ($\Delta\text{IE} = 0.0107$ eV) is within chemical accuracy, while the value calculated with DKH2 is closer to experiment. The CCSDT CBS value of 10.4977 eV ($\Delta\text{IE} = 0.0110$ eV) exhibits the same behavior. The IP-EOM-CCSD CBS value of 10.5548 eV ($\Delta\text{IE} = 0.0681$ eV) confirms the strong overestimation pattern at the CBS limit. The DKH2 contribution is −0.0121 eV, comparable to that of fluorine (−0.0127 eV), indicating that the scalar relativistic correction remains significant for the period 3 atom.

With the ANO-RCC basis sets, the CCSD(T) energy increases from 10.4106 eV (TZP, $\Delta\text{IE} = -0.0761$ eV) to 10.4203 eV (QZP, $\Delta\text{IE} = -0.0664$ eV) and 10.4499 eV (Full, $\Delta\text{IE} = -0.0368$ eV), the latter being within chemical accuracy. The CBS(T,Q) extrapolation yields 10.4281 eV ($\Delta\text{IE} = -0.0586$ eV), again less accurate than the Full value and outside chemical accuracy. CCSDT with the ANO-RCC-Full basis set yields 10.4518 eV ($\Delta\text{IE} = -0.0349$ eV), also within chemical accuracy. For IP-EOM-CCSD with the ANO-RCC basis sets, the ionization energy increases from 10.4317 eV (TZP, $\Delta\text{IE} = -0.0550$ eV) to 10.4474 eV (QZP, $\Delta\text{IE} = -0.0393$ eV) and 10.4946 eV (Full, $\Delta\text{IE} = 0.0079$ eV), the last two values being within chemical accuracy. The CBS(T,Q) yields 10.4589 eV ($\Delta\text{IE} = -0.0278$ eV), also within chemical accuracy.

For the Gaussian 16 results, B2PLYP underestimates the ionization energy by 0.1836 eV, while MP2 gives a deviation of −0.0362 eV, within chemical accuracy. CCSD(T) and QCISD(T) yield similar deviations of −0.0252 eV and −0.0266 eV, respectively, both within chemical accuracy. The G3 and CBS-QB3 methods yield deviations of −0.0230 eV and −0.0394 eV, respectively, also within chemical accuracy.

The performance of the tested methods for the phosphorus atom is illustrated in Figure 9. The figure highlights that the CCSD(T) and CCSDT methods are in excellent agreement with the experiment at the CBS-DK limit, with deviations of only −0.0016 and −0.0013 eV, respectively, while the IP-EOM-CCSD CBS values exceed the chemical accuracy limit due to the absence of explicit triple excitations.

For the **sulfur atom** (Table 9), the IE results obtained with the CCSD(T) and the aug-cc-pVXZ-DK basis sets show the largest basis-set dependence among all atoms studied. The QZ value of 10.2657 eV ($\Delta\text{IE} = -0.0943$ eV) and the 5Z value of 10.3085 eV ($\Delta\text{IE} = -0.0515$ eV) significantly underestimate the experimental value of 10.3600 eV, while the CBS value of 10.3540 eV ($\Delta\text{IE} = -0.0060$ eV) achieves chemical accuracy. CCSDT gives

slightly smaller deviations at all levels (-0.0905 , -0.0478 , and -0.0025 eV for QZ, 5Z, and CBS, respectively), with CCSDT/CBS-DK providing the closest agreement with the experiment among the methods used for sulfur. For IP-EOM-CCSD, the first ionization corresponds to the lowest root associated with the β electron removal. The QZ value ($\Delta IE = -0.0172$ eV) underestimates the IE, while the 5Z value ($\Delta IE = 0.0412$ eV) shifts to the opposite side and the CBS extrapolation increases the overestimation to 0.1025 eV, the largest IP-EOM-CCSD CBS-DK deviation among all atoms studied.

The aug-cc-pVXZ results yield higher ionization energy values, with the CCSD(T) CBS result being 10.3684 eV ($\Delta IE = 0.0084$ eV), within chemical accuracy. The CCSDT CBS is 10.3719 eV ($\Delta IE = 0.0119$ eV), also within chemical accuracy. The IP-EOM-CCSD aug-cc-pVQZ value of 10.3573 eV ($\Delta IE = -0.0027$ eV) is in nearly perfect agreement with the experiment, while the CBS value of 10.4773 eV ($\Delta IE = 0.1173$ eV) remains far from the threshold. The DKH2 contribution is -0.0142 eV, the largest among all atoms studied, consistent with sulfur having the highest nuclear charge.

For sulfur, the ANO-RCC basis sets show a slower convergence, with the largest difference between the QZP and Full results among the six atoms (0.1054 eV). The CCSD(T) values range from 10.1356 eV (TZP, $\Delta IE = -0.2244$ eV) to 10.1731 eV (QZP, $\Delta IE = -0.1869$ eV) and 10.2785 eV (Full, $\Delta IE = -0.0815$ eV), all being far from chemical accuracy. The CBS(T,Q) extrapolation yields 10.1989 eV ($\Delta IE = -0.1611$ eV), showing a significantly larger deviation than the Full result. CCSDT follows the same pattern, with ANO-RCC-Full at 10.2824 eV ($\Delta IE = -0.0776$ eV) and CBS(T,Q) at 10.2021 eV ($\Delta IE = -0.1579$ eV). For IP-EOM-CCSD, the ANO-RCC-Full value of 10.3736 eV ($\Delta IE = 0.0136$ eV) is within chemical accuracy, although this result likely reflects the cancellation of errors between the missing triple excitations and basis set incompleteness.

Finally, the B2PLYP computation yields a deviation of only 0.0196 eV, the closest to the experimental value among the Gaussian methods for this atom, while the MP2 underestimates the ionization energy by 0.1961 eV, the largest MP2 deviation among all atoms studied. CCSD(T) and QCISD(T) yield similar deviations of -0.0821 eV and -0.0807 eV, respectively, while G3 and CBS-QB3 underestimate the experimental value by 0.0909 eV and 0.1156 eV, respectively. Thus, sulfur and carbon are the only atoms for which none of the Gaussian composite methods achieve chemical accuracy.

Figure 10 shows the ΔIE values for the sulfur atom. The ANO-RCC basis sets underestimate the experimental value, although the Full contraction reduces the deviation. For IP-EOM-CCSD, both the aug-cc-pVXZ-DK and aug-cc-pVXZ basis sets show a change from negative ΔIE values at the QZ level to positive ΔIE values at the 5Z and CBS levels.

It should be noted that the CCSD(T) results obtained with Gaussian 16 using the aug-cc-pVQZ basis set are not directly comparable to ORCA CCSD(T)/aug-cc-pVQZ values, as the Gaussian calculations were performed with the default frozen-core approximation, while all ORCA computations included all electrons in the correlation treatment. The resulting differences range from approximately 0.002 eV for sulfur to 0.093 eV for carbon, depending on the relative contribution of core-valence correlation to the ionization energy of each atom.

The improvement obtained by using the iterative treatment of triple excitations in CCSDT, instead of the perturbative treatment used in CCSD(T), is very small for the ionization energies considered here. However, the computational cost increases substantially. For the atoms studied in this work, the CCSDT calculations were between 31 and 415 times more expensive than the corresponding CCSD(T) calculations performed with the same basis set. As representative examples, for the phosphorus atom with the aug-cc-pV5Z-DK basis set, the CCSDT calculation required approximately 45 h of wall-clock time, while the corresponding CCSD(T) calculation was completed in approximately 22 min. For the

fluorine atom with the same basis set, the CCSDT calculation required approximately 17 h, while the CCSD(T) calculation was completed in approximately 18 min. At the CBS limit, the difference between the CCSDT and CCSD(T) ionization energies remains very small for all six atoms. The mean absolute difference is 0.0019 eV, with values ranging from 0.0003 eV for P to 0.0036 eV for C. These differences are much smaller than the chemical accuracy threshold of 0.0434 eV. These results show that the perturbative treatment of triple excitations in CCSD(T) is sufficient for the calculation of the atomic ionization energies of the light elements considered in this work. Therefore, the additional computational cost of CCSDT is not justified for the atomic ionization energies studied here.

Table 10 summarizes the energies, types and degeneracies of the HOMO and HOMO-1 orbitals for the C, N, O, F, P, and S atoms, together with the HOMO-HOMO-1 energy gap, calculated at QCISD(T)/aug-cc-pVQZ level of theory. The spin character of HOMO confirms the behavior in the IP-EOM-CCSD calculations, indicating that for C, N, and P, the lowest ionization energy is associated with the α electron removal, while for O, F, and S, it comes from the β electron removal. The smallest HOMO-HOMO-1 gap is obtained for sulfur (0.98 eV), while the largest gap corresponds to phosphorus (4.47 eV).

Table 10. Energies, types, and degeneracies of the HOMO and HOMO-1 orbitals for the atoms C, N, O, F, P, and S and the HOMO-HOMO-1 energy gap calculated at QCISD(T)/aug-cc-pVQZ level of theory.

	C	N	O	F	P	S
HOMO type and degeneracy	α 2	α 3	β 1	β 2	α 3	β 1
HOMO-1 type and degeneracy	β 1	β 1	α 1	α 2	β 1	α 1
E_{HOMO} (a.u.)	−0.43903	−0.57090	−0.52173	−0.67998	−0.39209	−0.37946
$E_{\text{HOMO-1}}$ (a.u.)	−0.58357	−0.72606	−0.61167	−0.73174	−0.55635	−0.41562
$\Delta E_{\text{HOMO-HOMO-1}}$ (eV)	3.93	4.22	2.45	1.41	4.47	0.98

The overall performance of the computational methods is summarized in Table 11, which reports the mean absolute error (MAE) and mean signed error (MSE) for each method and basis set combination, averaged over the C, N, O, F, P, and S atoms.

The lowest MAE values were obtained with CCSDT and CCSD(T), in combination with the aug-cc-pVXZ-DK basis sets and CBS extrapolation. The CCSDT method gave an MAE of 0.0026 eV and an MSE of 0.0014 eV, while CCSD(T) gave an MAE of 0.0030 eV and an MSE of −0.0002 eV. These errors are more than one order of magnitude smaller than the chemical accuracy threshold of 0.0434 eV. In addition, the MSE values are close to zero, showing that the CBS-DK results do not present a systematic overestimation or underestimation of the experimental ionization energies. The small difference between CCSDT and CCSD(T) also confirms that the perturbative treatment of triple excitations in CCSD(T) is sufficient for the atoms studied in this work.

The aug-cc-pVXZ CBS results show slightly larger MAE values of 0.0095 eV for CCSD(T) and 0.0111 eV for CCSDT, with MSE values of 0.0095 eV and 0.0111 eV, respectively. The increase in both MAE and MSE relative to the DKH2 results reflects the absence of scalar relativistic corrections. For these atoms, the DKH2 correction lowers the computed ionization energies. However, the CBS results obtained with these basis sets remain well within chemical accuracy on average.

For IP-EOM-CCSD, the CBS extrapolation yields MAE = 0.0539 eV (MSE = 0.0539 eV) with DKH2 and MAE = 0.0636 eV (MSE = 0.0636 eV) without DKH2. In both cases, MAE equals MSE, indicating that the method systematically overestimates the ionization energy for all atoms at the CBS limit. At the finite basis set level, IP-EOM-CCSD reaches chemical accuracy on average for the aug-cc-pVQZ-DK (MAE = 0.0397 eV), aug-cc-pV5Z-DK (MAE = 0.0335 eV), aug-cc-pVQZ (MAE = 0.0330 eV), aug-cc-pV5Z (MAE = 0.0360 eV), and ANO-RCC-Full (MAE = 0.0377 eV) basis sets. This suggests that the finite-basis-set

incompleteness error compensates to some extent for the overestimation observed at the CBS limit, most likely related to the absence of triple excitations.

Table 11. Mean absolute error (MAE) and mean signed error (MSE) in eV, for each combination of method and basis set, averaged over C, N, O, F, P, and S atoms. The chemical accuracy threshold is 0.0434 eV (1 kcal/mol).

Method	Basis Set	MAE (eV)	MSE (eV)
CCSD(T)	aug-cc-pVQZ-DK	0.0606	−0.0606
	aug-cc-pV5Z-DK	0.0315	−0.0315
	SCF(5Z) + corr_CBS(Q,5)	0.0030	−0.0002
	aug-cc-pVQZ	0.0510	−0.0510
	aug-cc-pV5Z	0.0218	−0.0218
	SCF(5Z) + corr_CBS(Q,5)	0.0095	0.0095
	ANO-RCC-TZP	0.1470	−0.1470
	ANO-RCC-QZP	0.1123	−0.1123
	ANO-RCC-Full	0.0595	−0.0595
CCSDT	SCF(QZ) + corr_CBS(T,Q)	0.0820	−0.0820
	aug-cc-pVQZ-DK	0.0582	−0.0582
	aug-cc-pV5Z-DK	0.0295	−0.0295
	SCF(5Z) + corr_CBS(Q,5)	0.0026	0.0014
	aug-cc-pVQZ	0.0486	−0.0486
	aug-cc-pV5Z	0.0199	−0.0199
	SCF(5Z) + corr_CBS(Q,5)	0.0111	0.0111
	ANO-RCC-TZP	0.1441	−0.1441
	ANO-RCC-QZP	0.1097	−0.1097
IP-EOM-CCSD	ANO-RCC-Full	0.0571	−0.0571
	SCF(QZ) + corr_CBS(T,Q)	0.0796	−0.0796
	aug-cc-pVQZ-DK	0.0397	−0.0294
	aug-cc-pV5Z-DK	0.0335	0.0112
	CBS(Q,5)	0.0539	0.0539
	aug-cc-pVQZ	0.0330	−0.0197
	aug-cc-pV5Z	0.0360	0.0209
	CBS(Q,5)	0.0636	0.0636
	ANO-RCC-TZP	0.1344	−0.1344
B2PLYP	ANO-RCC-QZP	0.0885	−0.0831
	ANO-RCC-Full	0.0377	−0.0176
	CBS(T,Q)	0.0610	−0.0457
	aug-cc-pVQZ	0.3205	0.2500
	MP2	0.0811	−0.0558
	CCSD(T)	0.0746	−0.0746
	QCISD(T)	0.0631	−0.0631
G3	G3	0.0491	−0.0491
	CBS-QB3	0.0578	−0.0407

The ANO-RCC basis sets have larger MAE values, ranging from 0.1470 eV (TZP) to 0.0595 eV (Full) for CCSD(T). The MSE values are consistently negative, indicating a systematic underestimation due to the absence of diffuse functions. The CBS(T,Q) extrapolation (MAE = 0.0820 eV) does not improve over the Full result, as the extrapolation cannot compensate for the missing diffuse functions.

Across the Gaussian 16 methods that were used with the aug-cc-pVQZ basis set, B2PLYP exhibits the largest MAE (0.3205 eV) with a positive MSE (0.2500 eV), mostly influenced by the overestimation for fluorine. The composite methods G3 (MAE = 0.0491 eV, MSE = −0.0491 eV) and CBS-QB3 (MAE = 0.0578 eV, MSE = −0.0407 eV) provide the best performance among these methods, although none of them achieves chemical accuracy on average. For G3, the equality between MAE and MSE indicates a systematic underestimation for all six atoms. QCISD(T) (MAE = 0.0631 eV), MP2 (MAE = 0.0811 eV), and CCSD(T)

(MAE = 0.0746 eV) with the aug-cc-pVQZ basis set show larger deviations. For comparison, the corresponding ORCA CCSD(T)/aug-cc-pVQZ result gives a lower MAE of 0.0510 eV (MSE = −0.0510 eV). The difference between the Gaussian and ORCA CCSD(T) values can be attributed mainly to the frozen-core approximation employed in Gaussian calculations, while the ORCA results were obtained with all-electron correlation.

Overall, the statistical performance is summarized graphically in Figure 11, which shows MAE values averaged over the C, N, O, F, P, and S atoms. The CCSD(T) and CCSDT CBS extrapolations with aug-cc-pVXZ-DK have the lowest MAE values, well below the chemical accuracy threshold, while the ANO-RCC results exhibit consistently higher errors. Among the methods with the frozen-core approximation, G3 and CBS-QB3 provide the best performance; however, none of them achieves chemical accuracy on average.

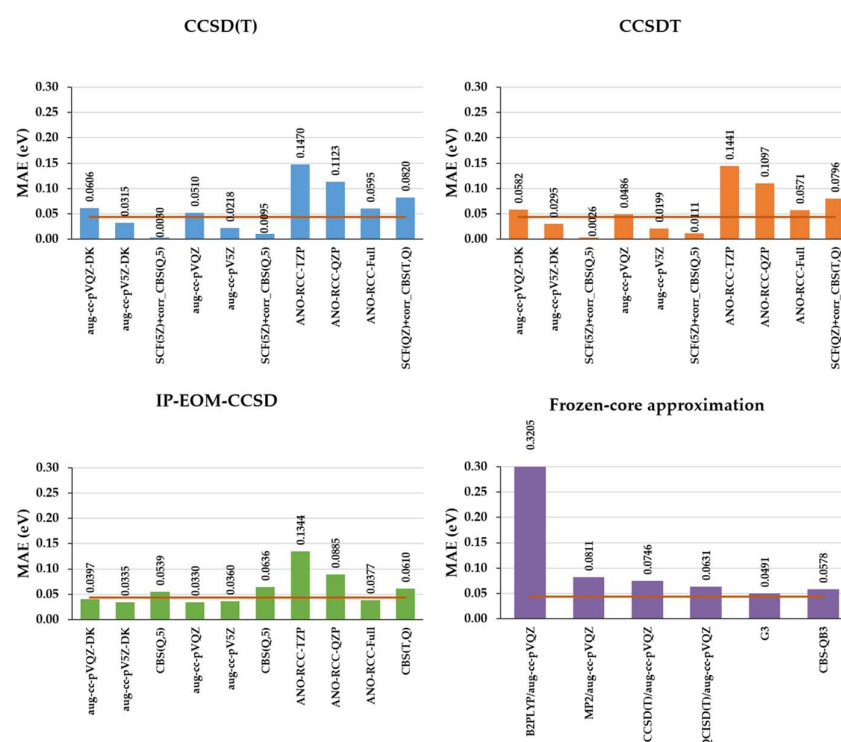


Figure 11. Mean absolute error (MAE, in eV) of the calculated ionization energies averaged over the C, N, O, F, P, and S atoms, obtained with CCSD(T), CCSDT, and IP-EOM-CCSD, and the methods employing frozen-core approximation. The horizontal line defines the interval of chemical accuracy.

4. Conclusions

In this work, the first ionization energies of the H, C, N, O, F, P, and S atoms were investigated using several quantum-chemical methods, with the aim of identifying computational protocols able to reproduce the experimental values within chemical accuracy. The methods included the electron propagator approaches OVGF and P3+, the coupled-cluster methods CCSD(T), CCSDT, and IP-EOM-CCSD, and the composite methods G3 and CBS-QB3. Several post-Hartree–Fock and DFT methods were also tested using the energy-difference approach. Atomic spin–orbit corrections were applied to all theoretical results, except for the final G3 and CBS-QB3 values, since these composite methods already include this contribution.

The OVGF and P3+ methods did not reach chemical accuracy on average for the six atoms (C, N, O, F, P, S). For all basis sets, OVGF performed better than P3+, while P3+ constantly underestimated the experimental ionization energies, as shown by the negative MSE. Among the tested basis sets, aug-cc-pVQZ gave the best results for both methods, followed by cc-pVQZ and 6-311+G(2df,p). Chemical accuracy was achieved

only in some cases, specifically with OVGF for phosphorus with the cc-pVQZ and aug-cc-pVQZ basis sets, and for oxygen and fluorine with the aug-cc-pVQZ basis set. The best agreement obtained with the propagator methods was found for the P atom, which has a large HOMO-HOMO-1 gap.

The CCSD(T) and CCSDT methods, used together with the aug-cc-pVXZ-DK basis sets and the CBS extrapolation scheme, provided the most accurate results. The corresponding MAE values were 0.0030 eV for CCSD(T) and 0.0026 eV for CCSDT, more than an order of magnitude smaller than the chemical accuracy threshold of 0.0434 eV. The difference between the two methods at the CBS limit was small for each atom, showing that the perturbative triples correction in CCSD(T) is enough for an accurate description of these ionization energies. Therefore, the much more computationally expensive iterative treatment of triple excitations in CCSDT did not bring significant improvement for the ionization energies of the atoms that were studied. Moreover, considering the much higher computational cost of CCSDT, CCSD(T) combined with CBS extrapolation represents the best compromise between the accuracy and the hardware resources.

The scalar relativistic contribution introduced through the DKH2 Hamiltonian, evaluated at the aug-cc-pV5Z level, was small but consistent. Its size increased with the atomic number, from about 0.0001 eV for hydrogen to approximately 0.0142 eV for sulfur. The atomic spin-orbit correction, derived from the NIST fine-structure data, ranged from 0.0016 eV for carbon to 0.0391 eV for phosphorus. For hydrogen, which is a one-electron system, the ionization energy is described at the Hartree-Fock level. All HF values obtained with the tested basis set families remained within chemical accuracy, and the CBS-QB3 gave the closest agreement with the experimental value.

The IP-EOM-CCSD method showed a different behavior. Since this method calculates the ionization energies directly from the ionized roots of the neutral reference state, it provides an independent comparison with the energy-difference results. At the finite basis set level, IP-EOM-CCSD reached chemical accuracy on average for the aug-cc-pVQZ-DK, aug-cc-pV5Z-DK, aug-cc-pVQZ, aug-cc-pV5Z, and ANO-RCC-Full basis sets due to the basis set incompleteness error, which partially compensated for the missing triple excitations. At the CBS limit, however, this effect was reduced, and the method systematically overestimated the experimental values.

The ANO-RCC basis sets showed a less uniform convergence than the aug-cc-pVXZ-DK basis sets. The CBS(T,Q) extrapolation based on the TZP and QZP contractions did not always improve the results and, in most cases, was less accurate than the Full result. This suggests that ANO-RCC basis sets may not be ideal for the calculation of these atomic ionization energies.

The Gaussian 16 results obtained with the default frozen-core approximation also showed that core-valence correlation is important for achieving chemical accuracy. Among these methods, G3 and CBS-QB3 gave the best overall agreement with the experiment, but none of them reached chemical accuracy on average over the six atoms, while the B2PLYP functional showed a particularly large overestimation for fluorine. The differences between the Gaussian CCSD(T)/aug-cc-pVQZ results and the corresponding all-electron ORCA values, ranging from approximately 0.002 eV for sulfur to 0.093 eV for carbon, confirm the importance of the core-valence correlation at this level of accuracy.

Overall, the results show that the most robust approach for the atomic ionization energies studied here is CCSD(T) with the aug-cc-pVXZ-DK basis sets, all-electron correlation, DKH2 scalar relativistic corrections, atomic spin-orbit corrections, and the CBS(Q,5) extrapolation scheme. The CCSDT results confirm the accuracy of the perturbative treatment of triple excitations in CCSD(T), while IP-EOM-CCSD provides a useful direct comparison. Thus, the consistency of the results obtained in this study supports the use of this protocol

as a reference atomic benchmark for the H, C, N, O, F, P, and S atoms. The results may also serve as a useful reference for future benchmark studies on atomic ionization energies, in which basis set convergence, electron correlation, relativistic effects, and spin–orbit corrections are relevant.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app16136386/s1>, Table S1: Spin-orbit corrections derived from the NIST fine-structure levels [48] for the C, N, O, F, P, and S atoms and their corresponding cations. The E_{LS} value was calculated using Equation (15). The ΔE_{SO} value represents the energy difference between E_{LS} and the lowest fine-structure level, as defined in Equation (16). The ΔIE_{SO} value was obtained as the difference between the cationic and neutral ΔE_{SO} values (Equation (17)). The SOC correction is reported in eV and was applied to the calculated ionization energies using Equation (18).

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Abbreviations

The following abbreviations are used in this manuscript:

EPT	Electron propagator theory
OVGF	Outer Valence Green's Function
P3+	Renormalized partial third-order quasiparticle
DFT	Density functional theory
MAE	Mean absolute error
MSE	Mean signed error
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
IE	Ionization energy
CCSD(T)	Coupled-cluster with single and double excitations and perturbative triples
CCSDT	Coupled-cluster with single, double, and triple excitations
IP-EOM-CCSD	Ionization Potential Equation-of-Motion Coupled-Cluster Singles and Doubles

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