Improving quasiparticle second order electron propagator calculations with the spin-component-scaled technique

Jonathan Romero^a, Jorge A. Charry^a, Hiromi Nakai^{b,c,d}, Andres Reyes^{a,*}

^a*Chemistry Department, Universidad Nacional de Colombia Av. Cra. 30 #45-03, Bogotá, Colombia*

^b*Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, Tokyo 169-8555, Japan*

^c*Research Institute for Science and Engineering, Waseda University, Tokyo 169-8555, Japan*

^d*CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

Abstract

A simple modification of the quasiparticle second order electron propagator (EP2) method based on the spin-component-scaled technique is proposed. In this new approach, the second order contributions to the self-energy of same and opposite spins are scaled by empirical parameters. Comparison with EP2 and higher order approaches for different sets of molecules reveals that the cost-free spin-component-scaled technique reduces average errors of EP2 up to 51%, thereby increasing its reliability and applicability for the calculation of electron binding energies in molecular systems.

Keywords: electron propagator theory, quasiparticle approximation, spin-component-scaled technique, ionization potential, electron affinity

1. Introduction

The electron propagator theory (EPT) and its equivalent formulations (one-electron Green's functions and equation-of-motion theories) are nowadays well established techniques for the accurate calculation of electron binding energies (EBEs), transition probabilities, total energies, and one-electron properties of molecules [1–18]. In EPT, the Hartree-Fock (HF) equations are generalized by introducing a non-local energy dependent correlation potential known as self-energy, and finally, correlated binding energies and orbitals (Dyson orbitals) can be obtained as eigenfunctions and eigenvalues of one-electron equations.

A number of self-energy operators have been proposed in EPT, however, those based on the quasiparticle approximation [4] are the most commonly used to compute EBEs. This approximation can be viewed as a correlated version of Koopmans' theorem, where the HF

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*Corresponding author

Email addresses: jromerof@unal.edu.co (Jonathan Romero), jacharrym@unal.edu.co (Jorge A. Charry), nakai@waseda.jp (Hiromi Nakai), areyesv@unal.edu.co (Andres Reyes)

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orbital energies are corrected by the diagonal elements of the self-energy matrix evaluated at a certain order of perturbation theory (PT) [1, 2, 15, 18].

Numerous studies employing quasiparticle approximations, summarized on references [13–18], have concluded that accurate calculations of EBEs can be reached by employing self-energy terms evaluated at third order, which is a highly demanding computational task [19]. For instance, the full-third order electron propagator (EP3) and the outer valence Green function (OVGF) approaches [10, 20, 21] require iteration steps that scale at ov^4 order (where o and v are the number of occupied and virtual orbitals, respectively) and have a fifth-power dependence on the number of basis functions. In the less demanding partial third order propagator (P3), proposed by Ortiz [12, 22], the calculation of molecular integrals with four virtual indexes is avoided, however, it still presents a o^2v^3 arithmetic scaling. In addition, calls to transformed integrals with one occupied and three virtual indexes become its rate limiting step. Modern implementations of OVGF and P3 methods bypass the storage of molecular integrals by using semi-direct integral transformation algorithms that exploit molecular symmetry to reduce computational time [21, 23]. Recently, a scheme to reduce the virtual orbital space [24] and the resolution-of-the-identity technique have been introduced [25] to increase the range of applicability of EPT. Although these advances have permitted to predict the photoelectron spectra of relatively large molecules such as macrocyclics, fullerenes and dinucleotides [26], third order propagator calculations on large systems are still highly computational demanding [19].

In contrast, the more affordable second order propagator (EP2) approximation presents a scaling of ov^2 , thereby permitting the study of larger molecular systems. Unfortunately, the reliability of the EP2 calculations is still poor when compared to that of P3 and OVGF [19].

Therefore, it is desirable to improve the accuracy of the EP2 method to calculate EBEs on large molecules without the inclusion of higher order terms. In this regard, the transition operator second order propagator (TOEP2) method [27] has succeeded. In this approach, second order calculations are performed using a modified HF reference state with a half-occupied orbital. This procedure incorporates relaxation effects that bring the accuracy of TOEP2 near to that of third order approaches for predictions of EBEs of valence orbitals [27]. Although the formal arithmetic scalings of TOEP2 and EP2 are virtually identical [19], TOEP2 method still faces some computational disadvantages not present in EP2 approach: slower convergence of the self-consistent field (SCF) procedure and the fact that only one EBE can be computed per single point calculation [17].

In this paper we propose to improve the quasiparticle second order propagator approach by exploiting the spin-component-scaled (SCS) technique proposed by Grimme [28]. The SCS procedure is based on the insight that low-order wave function expansions treat the correlation effects of electron pairs with opposite spin (OS) and same spin (SS) differently because of their uneven treatment at the underlying HF level [29]. To correct for this deficiency SS and OS correlation contributions are scaled. Under this scheme, improved versions of several correlated methods have been proposed [29], for instance: second order Møller-Plesset perturbation theory (MP2) [28, 30–33], third order Møller-Plesset perturbation theory (MP3) [34], singles-doubles configuration interaction (CISD) [35], configuration

interaction singles with perturbative doubles correction (CIS(D)) [36] and second-order approximate coupled-cluster (CC2) [37].

An outline of this paper is as follows: in Section 2 we briefly summarize the original SCS-MP2 method and present the new SCS-type of EP2 approach. In Section 3 we show the numerical assessment of the proposed methods comparing with other quasiparticle propagator methods for the calculations of EBEs. In Section 4 we summarize and provide concluding remarks.

2. Theory and Implementation

The spin component technique[28–37], originally proposed by Grimme [28] separates the MP2 correction energy into *parallel* (SS) and *anti-parallel* (OS) contributions:

$$E^{(2)} = E_{ss}^{(2)} + E_{os}^{(2)} \quad (1)$$

Where:

$$E_{ss}^{(2)} = 1/2 \sum_{ij} E_{ij} + 1/2 \sum_{IJ} E_{IJ} \quad (2)$$

$$E_{os}^{(2)} = \sum_{iI} E_{iI} \quad (3)$$

$$E_{ij} = \sum_{ab} (T_{ij}^{ab} - T_{ij}^{ba}) (ia|jb) \quad (4)$$

$$E_{IJ} = \sum_{AB} (T_{IJ}^{AB} - T_{IJ}^{BA}) (IA|JB) \quad (5)$$

$$E_{iI} = \sum_{aA} T_{iI}^{aA} (ia|IA) \quad (6)$$

where $I, J, \dots$ ($A, B, \dots$) stand for occupied (virtual) orbitals of electrons with spin β and $i, j, \dots$ ($a, b, \dots$) stand for occupied (virtual) orbitals of electrons with spin α . Electron repulsion integrals are written using Mulliken's notation. The T letters denote the corresponding second order amplitudes:

$$T_{ij}^{ab} = \frac{(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad T_{iI}^{aA} = \frac{(ia|IA)}{\epsilon_i + \epsilon_I - \epsilon_a - \epsilon_A} \quad T_{IJ}^{AB} = \frac{(IA|JB)}{\epsilon_I + \epsilon_J - \epsilon_A - \epsilon_B} \quad (7)$$

The idea behind the SCS technique is that non-exact T amplitudes describe the OS and SS interactions differently because of their different treatment at the underlying HF level [28, 29]. This failure is systematically corrected by applying a separate scaling of the two contributions. Then, equation 1 is modified as:

$$E^{(2)} = p_{ss} E_{ss}^{(2)} + p_{os} E_{os}^{(2)} \quad (8)$$

where p_{ss} and p_{os} scale the SS and OS contributions to the total MP2 correlation energy with values that are smaller and larger than 1, respectively [28]. Values of p_{ss} and p_{os}

are generally determined by parametrization against highly correlated approaches, such as coupled-cluster with single and double and perturbative triple excitations CCSD(T) or configuration iteration (CI) method [29]. The SCS parameters have been interpreted in terms of a generalization of the Feenberg scaling, as proposed by Szabados [32] and have been theoretically derived from an alternative version of the Møller-Plesset (MP) proposed by Fink [33]. In this theory, known as S2-MP, the unperturbed Hamiltonian is defined to contain the ordinary Fock operator and spin operators that act either on the occupied or the virtual spaces. Consequently, contributions from the singlet-coupled and triplet-coupled doubly excited configurations are scaled by a couple of factors denoted by p_S and p_T , respectively, enhancing the description of the perturbed wave function. Values of p_S and p_T are related with p_{ss} and p_{os} by simple formulas.

Following Grimme's approach, we propose a separation of the second order self-energy correction [18] into its spin-components based on the separation shown in Eq.1 for the MP2 total energy correction. For electronic systems containing electrons with spins α and β , the energy of the spin-orbital p , E_p , calculated using the second order quasiparticle approximation can be expressed as [38]:

$$E_p^\alpha = \epsilon_p^\alpha + \Sigma_{pp}^{\alpha-\alpha(2)}(E_p^\alpha) + \Sigma_{pp}^{\alpha-\beta(2)}(E_p^\alpha) \quad \text{for } p \in \alpha \quad (9)$$

Note that $\alpha-\alpha$ (or $\beta-\beta$) and $\alpha-\beta$ represent SS and OS contributions, respectively. Consequently, the above equations can be viewed as:

$$E_p = \epsilon_p + \Sigma_{pp}^{ss(2)}(E_p) + \Sigma_{pp}^{os(2)}(E_p) \quad (10)$$

and we can propose a SCS quasiparticle second order self-energy as:

$$E_p = \epsilon_p + p_{ss} \Sigma_{pp}^{ss(2)}(E_p) + p_{os} \Sigma_{pp}^{os(2)}(E_p) \quad (11)$$

where the formulas for the second order self-energy terms are given by:

$$\Sigma_{pp}^{ss(2)}(E_p) = \sum_{a,i>j \in \alpha} \frac{|(pi||aj)|^2}{E_p + \epsilon_a - \epsilon_i - \epsilon_j} + \sum_{i,a>b \in \alpha} \frac{|(pa||ib)|^2}{E_p + \epsilon_i - \epsilon_a - \epsilon_b} \quad \text{for } p \in \alpha \quad (12)$$

$$\Sigma_{pp}^{os(2)}(E_p) = \sum_{i \in \alpha} \sum_{I, A \in \beta} \frac{|(pi||AI)|^2}{E_p + \epsilon_A - \epsilon_i - \epsilon_I} + \sum_{a \in \alpha} \sum_{I, A \in \beta} \frac{|(pa||IA)|^2}{E_p + \epsilon_I - \epsilon_a - \epsilon_A} \quad \text{for } p \in \alpha \quad (13)$$

We modified the propagator module implemented in the LOWDIN program [38–40] to introduce factors p_{ss} and p_{os} in the calculation of quasiparticle second order EBEs. Although several authors have proposed different values of p_{ss} and p_{os} based on different parametrizations and alternative derivations of perturbation theory [29], we opted to work with the parameters originally proposed by Grimme for his SCS-MP2 method: $p_{ss} = 1/3$ and $p_{os} = 6/5$ [28], as a first approximation. We have also utilized the parameters proposed by Jung et al. for their scaled opposite spin (SOS) MP2 method [30, 31] $p_{ss} = 0.0$ and

$p_{os} = 1.3$. These parameters have proven to significantly improve the calculation of molecular properties [28–31]. The proposed modified EP2 approaches are named as SCS-EP2 and SOS-EP2, respectively. We point out that the proposed approaches, as their SCS-MP2 [28] and SOS-MP2 [30, 31] counterparts, can be understood as first-principle methods (like DFT) which include a few global parameters that are motivated by theoretical arguments [28, 29, 32, 33] and this differentiates them from other attempts of parametrization of the self-energy [41] and semiempirical propagator approaches [17].

3. Numerical Assessments

Here we determine the accuracy and applicability of the SCS-EP2 and SOS-EP2 approaches contrasting their performance with those of regular EP2 and higher order quasiparticle approximations in the calculation of EBEs of valence orbitals. Calculations are performed on sets of singlet and doublet molecules commonly employed to assess the performance of electron propagator methods [12, 19, 22, 27]. EP2, SOS-EP2 and SCS-EP2 calculations were run with the modified version of the LOWDIN program [38–40]. P3 [12] and CCSD(T) calculation, employed for comparison, were run with the GAUSSIAN suite of programs [42]. EBEs calculated using CCSD(T) were determined by taking the difference between the total CCSD(T) energy of the ionized and the initial state (only for first ionization energies). In post-Hartree Fock calculations all the molecular orbitals were considered in the integral transformation step.

3.1. EBEs of neutral singlets

SOS-EP2 and SCS-EP2, EP2, TOEP2 [27], OVGF (B version) [10, 20, 21], EP3 and P3 [12] procedures were employed to calculate 23 EBEs of B_2H_6 , CH_4 , C_2H_4 , HCN , NH_3 , N_2 , CO , H_2CO , H_2 , HF and F_2 . Absolute errors with respect to experimental vertical ionization energies [43] are presented in Table 1 along with the experimental data and mean absolute errors (MAEs). All calculations reported in this table were performed with a cc-pVTZ basis set on experimental geometries [44].

A first inspection of Table 1 reveals that SOS-EP2 and SCS-EP2 methods are more accurate, with MAEs of 0.37 and 0.43 eV respectively, than the regular EP2, with a MAE of 0.63 eV. At this point it must be pointed out that these improvements in accuracy are reached at not extra computational costs. In the case of SCS-EP2 calculations, costs are identical to those of regular EP2 ones since computations are performed multiplying the total self-energy contributions by the corresponding parameters. As to SOS-EP2 calculations, extra computational savings are achieved since only Coulomb-type integrals are required [30].

We now compare the performance of SOS-EP2, SCS-EP2 and TOEP2 approaches. We find that the former procedures present slightly larger MAEs than the latter. In spite of this SOS-EP2 and SCS-EP2 method do not present the computational disadvantages of TOEP2, namely, slower convergence of the SCF procedure because of fractional occupations and that a single EBE is computed per SCF calculation.

Table 1 also shows that SCS-EP2 and SOS-EP2 methods produce slightly smaller MAEs than EP3 and larger MAEs than OVGF and P3 methods, especially for valence orbitals of

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3 molecules containing fluorine atoms. Nevertheless, SCS-EP2 and SOS-EP2 are much more
4 computational efficient than any of these third order approaches. Consequently, they become
5 attractive options to tackling large molecules where, for instance, the highest accuracy is
6 not required to assign photoelectron spectra [15].

7
8 An inspection of average errors presented on Table 1 reveals that for 17 of the 23 cal-
9 culated EBEs, SOS-EP2 and SCS-EP2 approaches produce smaller errors than the regular
10 EP2. In the cases where the errors are larger, such as for some EBEs of B₂H₆, HCN, C₂H₄,
11 N₂ and CO, third order approximations also display larger errors than EP2. These larger
12 deviations in the calculation of the EBEs, are not necessarily a consequence of the spin
13 scaling procedure but presumably a result of the poor description of shakeup effects within
14 the quasiparticle approximation [45–47].

15
16 Results presented above unveil the potential of the spin-scaling technique to improve
17 EP2 calculations in singlet neutral molecules. To reach a more thorough assessment of the
18 performance of the spin-scaling technique we compared first vertical ionization energies (IEs)
19 calculated with Koopmans’, EP2, SOS-EP2, SCS-EP2, P3 propagator approaches on a set of
20 70 singlet neutral molecules taken from the G2 set [48]. In these calculations, the final state
21 corresponds to a doublet cation. The diversity of bonding patterns in this set presents a
22 convenient standard for testing the performance of propagator methods [22]. Geometries on
23 the G2 set were optimized at MP2(Full)/6-31G(d) level of theory. Propagator calculations
24 were carried out using a cc-pVTZ basis set. Values of IEs calculated using CCSD(T) are
25 also presented as a reference to estimate errors introduced by basis set insufficiency, neglect
26 of relativistic and magnetic effects, among others. The complete list of results is collected
27 in the supporting information. Figure 1 presents the distribution of errors with respect to
28 experimental values for all the tested methods. Table 2 shows a statistical analysis of these
29 distributions.

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31 As shown in Figure 1, Koopmans’ theorem presents a bimodal distribution with errors
32 ranging from -0.69 eV to 3.20 eV and a mean value located at 0.70 eV, thus indicating that
33 Koopmans’ theorem overestimates IEs. On the other hand, EP2 method underestimates
34 values of IEs, as evidenced by the distribution ranging from -1.7 to 0.7 eV with a mean
35 value located at -0.48 eV. Distribution of errors for SOS-EP2 and SCS-EP2 show significant
36 improvement over the regular EP2: we observe that values of means and medians for the
37 SOS-EP2 and SCS-EP2 methods, presented in Table 2, are less negative than those of regular
38 EP2. This fact indicates that the SCS procedure corrects the tendency of EP2 calculations
39 to underestimate IEs.

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41 An analysis of the highly symmetric distribution of errors of P3 method reveals that
42 92.3% of the predictions have absolute errors under 0.5 eV (97.1% for CCSD(T) calcula-
43 tions). The percentages of molecules within the same range for the SOS-EP2 and SCS-EP2
44 approaches are 86.2% and 80.0% respectively (57.1% for regular EP2). We identified the
45 nature of systems presenting absolute errors over 0.5 eV for the SCS approaches, finding
46 that they mainly correspond to highly polar small molecules containing fluorine and oxygen
47 atoms. For this type of systems third order contributions are large [12, 22] and SCS methods
48 produce modest improvements over the EP2 method.

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50 Finally, we present in Table 3 MAEs for the different approaches considered in this study.

We observe that the SOS-EP2 and SCS-EP2 methods reduce the MAEs of EP2 by 0.20 and 0.26 eV, which corresponds to reductions of 40% and 51%. We have also found that the SCS-EP2 and the SOS-EP2 methods present MAEs only 0.12 and 0.06 eV larger than the P3 approach. Compared to the CCSD(T) approach, MAEs of SCS-EP2, SOS-EP2 and P3 approaches are 0.18, 0.12 and 0.06 eV larger. These results demonstrate that the reliability of EP2 calculations can be increased by exploiting the SCS technique. This procedure could become especially important to study the photoelectron spectra of large closed-shell molecules where third order calculations are much more demanding.

3.2. EBEs of neutral doublets

The IEs of 13 doublet neutral molecules from the G2 set [48] were calculated with the same procedure employed in the previous section. As shown in Table 3 the MAE of the EP2 method for the transition between the neutral doublet and the cationic singlet is 0.30 eV and those of SOS-EP2 and SCS-EP2 methods are 0.25 and 0.30 eV, respectively. A similar MAE is observed for P3 (0.24 eV). In contrast, MAE for CCSD(T) calculation is 0.14 eV. The small improvements obtained by propagator theory could be attributed to the unconvergence of perturbative series for the open-shell initial state, as observed for SCS MP2 calculations [29].

Alternatively, the IEs of doublet systems can be estimated as electron affinities (EA) of the corresponding cationic singlet, where the neutral doublet corresponds to the final state of the transition. Results obtained with this procedure are also summarized in Table 3. MAEs of the EP2, SCS-EP2, SOS-EP2, P3 and CCSD(T) methods are 0.43, 0.21, 0.26, 0.25 eV and 0.14 eV respectively. As observed, SCS approaches reduce MAEs of regular EP2 51% and 37%, respectively. The magnitudes of these reductions are similar to those observed for neutral systems, suggesting that the SCS technique displays a better performance when the initial electronic state is a singlet.

3.3. EBEs of anionic singlets

Propagator calculations were performed for the IEs of 12 singlet anions. In these calculations an aug-cc-pVTZ basis set was used as recommended in Ref.[49]. As shown in Table 3 the MAEs of SOS-EP2 and SCS-EP2, 0.82 and 0.79 eV respectively, are slightly better than the MAE of regular EP2, 0.89 eV. MAEs for EP2 is larger than those of Koopmans' theorem, as previously observed in Ref.[49]. CCSD(T) and P3 predictions improve those of Koopmans' theorem, although MAEs are larger than 0.2 eV. Ortiz has pointed out that quasiparticle approximations do not suffice to describe valence ionizations of some closed-shell anions [15, 18], and that non-diagonal renormalized approximations need to be employed [46, 50]. In this regard we are exploring the application of the SCS technique to non-diagonal second order self-energy approaches.

4. Conclusions and perspectives

We proposed a modified quasiparticle second order propagator approach based on the cost-free SCS technique [29]. The new SOS-EP2 and SCS-EP2 methods, were utilized to

compute EBEs of singlet and doublet molecular systems. Results presented in this study demonstrate that SOS-EP2 and SCS-EP2 are more accurate than the regular EP2 approach, reducing its average error up to 51%. Comparison with higher order approximations allowed us to establish that SOS-EP2 and SCS-EP2 methods can be used with semi-quantitative and quantitative purposes, presenting average absolute errors of 0.25 and 0.31 eV, respectively, for the studied set of closed shell molecules. The proposed SOS-EP2 and SCS-EP2 approaches have the same computational costs of the regular EP2 method, thus becoming efficient alternatives for the assignment of photoelectron spectra of large closed-shell molecules.

Future work along this line will be devoted to the application of the SCS technique to a non-diagonal second order approach and the development of SCS EPT methods including third order terms, aiming at increasing the accuracy on the calculation of EBEs. We are also exploring different alternatives for the determination of optimal values for p_{os} and p_{ss} by parametrization against higher order EPT results.

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Figure 1: Distribution of errors for Koopmans', EP2, SOS-EP2, SCS-EP2 and P3 calculations on a set of 70 molecules from the G2 set. The cc-pVTZ basis set was used.

Table 1: Absolute errors with respect to experimental values of the predicted EBEs using different quasiparticle propagator approaches. Values enclosed in boxes denote cases where the deviations of SOS-EP2 and SCS-EP2 are larger than those of EP2. Values in eV.

Molecule	Orbital	Expt. ^a	EP2	SOS-EP2	SCS-EP2	P3 ^b	EP3 ^b	OVGF ^b	TOEP2 ^b
B ₂ H ₆	1b _{3g}	11.9	0.25	0.60	0.48	0.24	0.40	0.46	0.40
CH ₄	1t ₂	14.4	0.30	0.02	0.09	0.18	0.03	0.08	0.06
C ₂ H ₄	1b _{3u}	10.63	0.32	0.13	0.19	0.08	0.11	0.15	0.02
	1b _{3g}	13.15	0.37	0.13	0.04	0.17	0.02	0.09	0.15
	3a _g	14.9	0.45	0.05	0.12	0.01	0.08	0.13	0.04
	1b _{2u}	15.9	0.03	0.41	0.26	0.21	0.51	0.27	0.35
	2b _{1u}	19.2	0.13	0.42	0.32	0.24	0.59	0.41	0.49
HCN	1π	13.61	0.05	0.18	0.14	0.35	0.03	0.00	0.39
NH ₃	3a ₁	10.8	0.62	0.35	0.44	0.07	0.21	0.06	0.15
N ₂	1π _u	16.98	0.19	0.26	0.23	0.20	0.53	0.35	0.40
	3σ _g	15.6	0.53	0.10	0.25	0.33	0.32	0.25	0.13
	2σ _u	18.78	0.61	0.24	0.37	0.52	1.11	0.30	0.19
CO	5σ	14.01	0.04	0.26	0.19	0.26	0.03	0.16	0.12
	1π	16.91	0.43	0.26	0.32	0.13	0.45	0.16	0.03
H ₂ CO	2b ₂	10.9	0.94	0.39	0.58	0.00	0.63	0.14	0.52
H ₂ O	1b ₁	12.78	1.27	0.87	1.01	0.29	0.30	0.17	0.49
	1a ₁	14.74	0.92	0.52	0.65	0.03	0.60	0.17	0.18
	1b ₂	18.51	0.34	0.05	0.08	0.23	0.63	0.36	0.17
HF	1π	16.19	1.48	0.98	1.15	0.25	0.64	0.17	0.53
	3σ	20	1.05	0.66	0.79	0.16	0.48	0.16	0.36
F ₂	1π _g	15.83	1.62	0.80	1.08	0.21	0.69	0.25	0.94
	3σ _g	21.1	0.67	0.19	0.35	0.06	0.05	0.10	0.04
	1π _u	18.8	1.51	0.56	0.88	0.09	1.32	0.21	0.70
MAE^c			0.63	0.37	0.43	0.19	0.42	0.20	0.30

^a. Experimental values from Ref.[43]. ^b. Values computed with based on EBEs reported on Ref.[27] ^c. Mean absolute error with respect to experimental values.

Table 2: Statistical analysis of the distribution of errors for Koopmans’ theorem (KT), EP2, SCS-EP2, SOS-EP2, P3 and CCSD(T) calculations for the tested molecules. Values in eV.

	KT	EP2	SCS-EP2	SOS-EP2	P3	CCSD(T)
Minimum	-0.69	-1.58	-1.24	-1.08	-0.85	-0.82
1st Quarter	-0.05	-0.72	-0.42	-0.34	-0.10	-0.12
Median	0.83	-0.36	-0.17	-0.07	0.06	-0.02
Mean	0.70	-0.48	-0.26	-0.14	0.06	-0.02
3rd Quarter	1.26	-0.18	-0.04	0.03	0.20	0.05
Maximum	3.20	0.52	0.67	0.82	0.59	0.69

Table 3: Mean absolute errors (MAEs) for Koopmans’ theorem (KT), EP2, SOS-EP2, SCS-EP2, P3 and CCSD(T) calculations on the testing set of molecules, radicals and anions from the G2 set. The cc-pVTZ basis set was used.

Systems	KT	EP2	SCS-EP2	SOS-EP2	P3	CCSD(T)	n
Neutral singlets	0.82	0.51	0.31	0.25	0.19	0.13	70
Neutral doublets ^a	1.04	0.30	0.25	0.30	0.24	0.14	12
Neutral doublets ^b	1.40	0.43	0.21	0.26	0.25	0.14	12
Anionic singlets	0.52	0.80	0.72	0.68	0.36	0.25	12

^a Neutral doublet as initial state.

^b Cationic singlet as initial state.

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