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Short Communication

Calculation of Vertical Ionization Potentials of Ketene by Perturbation Corrections to Koopmans' Theorem

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The vertical ionization potentials of ketene are calculated by perturbation corrections to Koopmans' theorem. The present results are compared with those from the pseudonatural orbital coupled electron pair approach and the experimental values.

Key words: Ketene, vertical ionization potentials of ~

1. Introduction

In the past few years, various methods[1] have been used to calculate vertical ionization potentials (VIP's) beyond the accuracy of Koopmans' theorem [2]. Our straightforward application [3, 4] of Rayleigh–Schrödinger perturbation theory (RSPT) led to computed VIP's which are of comparable accuracy to those obtained with Green's functions [1] when the basis sets are the same or nearly the same[2]. Recently, Hernández and Langhoff [6] found that a) RSPT and Green's functions (with no energy iterations) should give *identical* second- and third-order corrections to Koopmans' theorem, and that b) the effects of energy iterations on the Green's function results are generally small. Therefore, the major difference between these two approaches lies in the choice of basis set which is determined by the amount of computer time available and by the accuracy required.

In contrast, the advantages of partial cancellation of computational errors is absent in configuration-interaction (CI) studies of VIP's. For example, the maximum error of the calculated VIP's for N_2 is 0.90 eV from ΔCI studies using a basis set of ($4s2p1d$) Slater-type orbitals [7], while our maximum error [4] from

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[1] See Ref. [1] for a brief review.

[2] The perturbation corrections to Koopmans' theorem recently obtained by diagrammatic many-body RSPT [5] are essentially identical to our results [3].

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Table 1. Calculated energies (in hartrees) of ketene

Ref.	Basis set		$E+150$
This work	[4s2p/2s]	SCF	−1.6719[b]
		$\mathcal{E}$[a]	−1.9372[b]
		$E(3)$	−1.9639
		E^{GA}	−1.9640
Snyder and Basch[c]	[4s2p/2s]	SCF	−1.6595[b]
Dykstra and Schaefer[d]	[4s2p1d/2s1p]	SCF	−1.7555[b]
Hall, Maier, and Rosmus[e]	[6s3p1d/3s1p]	SCF	−1.7646[b]
		PNO-CI	−2.0507[b]
		CEPA	−2.0816

[a] Scaled energy expectation value.

[b] Upper bound.

[c] Ref. [15]. They used a different double-zeta basis set.

[d] Ref. [18]. The energy is for the calculated equilibrium geometry.

[e] Ref. [14].

RSPT is 0.59 eV with (4s2p) Slater-type orbitals and 0.50 with [4s2p1d] contracted Gaussian-type orbitals. For the water molecule, if one uses the experimental VIP's of Brundle and Turner [9] as corrected by Meyer [10], instead of the observed values of Potts and Price [11], the maximum error of the calculated VIP's from ΔCI studies [12] using a basis set of (5s4p2d/3s1p) Slater-type orbitals is 0.48 eV, and that from ΔPNO-CI calculations [10] using [11s7p4d1f/5s1p] Gaussian-type is 0.44 eV, compared to 0.36 eV from our RSPT results using a smaller set of [4s2p1d/2s1p] contracted Gaussian-type orbitals [3]. The ΔPNO-CEPA (pseudo-natural orbital coupled electron pair approximation) method of Meyer [10] reduces the maximum error of the VIP's to 0.30 eV, with the extensive basis set. In short, it seems that the indirect methods of ΔCI, ΔPNO-CI and ΔPNO-CEPA are less cost-effective than the direct methods of RSPT, Green's functions, and equation-of-motion [13].

Recently [14], the photoelectron spectrum of ketene has been observed and compared with VIP's calculated by ΔPNO-CEPA using a basis set of contracted

Table 2. Vertical ionization potentials (in eV) of ketene

Obs.		Koopmans' theorem				$\Delta E(3)$	$\Delta(E^{GA})$	ΔCEPA
[14]		This work	[15]	[18][a]	[14]	This work	This work	[14]
9.8	$^2B_1$	9.98	9.97	10.00	9.95	9.18	9.14	9.50
14.2	$^2B_2$	15.32	15.31	15.26	15.33	14.37	14.23	14.46
15.0	$^2B_1$	17.88	17.88	17.46	17.55	16.06	15.56	15.08
16.3	$^2B_2$	18.22	18.21	17.89	17.91	16.69	16.61	16.79
16.8	$^2A_1$	18.51	18.51	18.59	18.51	16.91	16.70	17.04
18.2	$^2A_1$	20.51	20.51	20.67	20.68	19.44	18.44	18.57

[a] At the calculated equilibrium geometry.

Gaussian-type orbitals of triple zeta plus polarization functions. The maximum error of the first six VIP's is 0.49 eV (see Table 2). In this work, these six VIP's are calculated by RSPT using a smaller basis set of double-zeta contracted Gaussian-type orbitals, and compared with the ΔPNO-CEPA results.

2. Calculations and Results

The detailed method of computing perturbation corrections to Koopmans' theorem has been given elsewhere [3]. The nuclear coordinates used in this work are taken from Snyder and Basch [15]. The basis set is the standard Huzinaga–Dunning [16, 17] set of contracted double-zeta Gaussian-type orbitals.

The quality of the basis set is indicated in Table 1, in which some calculated energies of ketene are presented and compared with those of other workers. Although only 9% of all the possible terms is included in $\psi^{(1)}$, for the choice of the truncation criterion $T=2.6$, the correlation energy accounted for by $\psi^{(1)}$ in terms of $\mathscr{E}-E(\mathrm{SCF})$, or $E^{\mathrm{GA}}-E(\mathrm{SCF})$, is 92 to 93% of $E(\mathrm{PNO-CI})-E(\mathrm{SCF})$, or $E(\mathrm{CEPA})-E(\mathrm{SCF})$ respectively.

The results of VIP's calculated in this work are summarized in Table 2. The errors in Koopmans' VIP's are very similar. Our $\Delta(E^{\mathrm{GA}})$ VIP's are better than the $\Delta E(3)$ results, especially for the second $^2B_1$ and the second $^2A_1$ cationic states. This is related to the larger values of $\langle 1|1\rangle=0.396$ and 0.366 respectively, compared to values of 0.114 for the parent and 0.165 for the first $^2B_1$ state, for example. Finally, our $\Delta(E^{\mathrm{GA}})$ results compare very favorably with those of Hall, Maier, and Rosmus [14] using ΔPNO-CEPA with a much larger basis set. While the excited cationic states (as close together as 0.5 to 0.8 eV) cannot be unambiguously assigned by our calculated VIP's with a maximum error of 0.66 eV, the assignment based on ΔPNO-CEPA with a maximum error of 0.49 eV is not much more certain. For problematic assignments, one would use larger basis sets and/or include vibrational structures [1].

3. Discussions

The present results, summarized in Table 2, seem to support the observation that the indirect methods of ΔCI, ΔPNO-CI, and ΔPNO-CEPA are less cost-effective than the direct methods of RSPT, Green's functions, and equation-of-motion. The reason is believed to be the absence of partial cancellation of computational errors. However, preliminary studies [19] indicate that such partial cancellation can be put into ΔCI studies of VIP's, provided one uses the more convenient frozen orbitals of the parent molecule in computing the CI energies of the cations. Consequently, we expect that future ΔCI calculations of VIP's will be competitive, in terms of cost-effectiveness, with the direct methods of RSPT, Green's functions, and equation-of-motion[3].

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[3] Our ΔCI results on H_2O, N_2, C_2H_2 and HCN using double-zeta and double-zeta plus polarization functions basis sets of contracted Gaussian-type orbitals are very encouraging [19], in contrast to the recent calculations of Hase *et al.* [20].

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