Theoret. Chim. Acta (Berl.) 45, 185–195 (1977)

THEORETICA CHIMICA ACTA

Calculation of Vertical Ionization Potentials of H_2O and Ne by Many-Body Rayleigh-Schrödinger Perturbation Theory*

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The vertical ionization potentials of H_2O and Ne are calculated by many-body Rayleigh-Schrödinger perturbation theory up to third order. The comparison of the present method with the other approaches is done.

Key words: Ionization potentials – Many-body perturbation theory

1. Introduction

In recent papers [1–25] various techniques are employed to interpret photoelectron spectra. Koopmans' theorem [26] (the negative value of the Hartree-Fock orbital energy $-\varepsilon_h$), which is often used to interpret the ionization potentials does not serve as an appropriate tool in some cases.

The true ionization potential (I_H) is given by

$$I_H = -\varepsilon_h - R + C \tag{1}$$

where R stands for reorganization and C for correlation effects, respectively. Usually these effects cancel each other almost exactly and Koopmans' theorem is a good approximation to ionization potential. For some cases this cancellation is not exact and the effects which are known as Koopmans' defect and breakdown of Koopmans' theorem appear. In order to include the reorganization and correlation effects we have to go beyond the Hartree-Fock (HF) approximation. The techniques based on Green's functions [1–11], many-body Rayleigh-Schrödinger perturbation theory (MB-RSPT) [12, 13], the equation of motion method [14–18], the natural

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* This paper is dedicated to the memory of our friends and colleagues Dr. Jarka Surá and Dr. Marta Černayová who died in a plane crash on the 28th of July 1976 in Bratislava.

transition orbitals method [19, 20], the ordinary Rayleigh-Schrödinger perturbation theory [21, 22], the superoperator technique [23], the density matrices and natural functions [24] and PNO-CI method [25] were used to calculate the corrections to Koopmans' theorem which are due to reorganization and correlation effects. These different approaches are all by no means distinct, as numerous interrelationships among them may be demonstrated but each provides its own viewpoint which suggests different computational characteristics. Among the mentioned methods the Green's function approach [6–10] seems to be the most elegant and effective one and it seems natural that it is this approach to which all other approaches are compared. The aim of this paper is to perform the calculation of vertical ionization potentials (VIP's) by time-independent MB-RSPT [12] and to demonstrate that this method leads to the same results as the Green's function approach. We would like to show in this paper also that the Rayleigh-Schrödinger perturbation expressions for direct calculation of the ionization potentials may be obtained in a rather simple way without involvement of the Green's function formalism. For the calculations we have chosen the same systems as studied by the Green's function method [8, 9] and essentially the same basis. We want to compare our direct calculation of $2a_1$ ionization potential of H_2O molecule with the Green's function approach since this state does not belong to the Σ_{-1}, Σ_{+1} interval [8] as well as to test the effect of inclusion of all virtual orbitals in perturbation expansion.

The diagrammatic technique which represents a very powerful tool to study the correlation energy to various orders and various forms of MB-RSPT (different partitioning of the Hamiltonian) is used for ground state [27–30] as well as for excitation processes [29, 30, 38]. This technique gives us the possibility to see the dominant "diagrammatic" contributions which can then be summed up to all orders of perturbation theory. To study the corrections to Koopmans' ionization potentials from this point of view is also the aim of this paper.

2. Theory

The general features of the theory for calculation of ionization potentials by time-independent MB-RSPT were formulated in our paper [12]. For the completeness we briefly recapitulate the theory here in its very simple form. The formulation of the theory in our paper [12] was given in quasi-degenerate MB-RSPT. The formulation in this paper we recapitulate for simplicity in non-degenerate time-independent MB-RSPT. We have used a similar formulation as that demonstrated in [30], which is equivalent to the case $P_0 = |\Phi_H\rangle\langle\Phi_H|$ (Eq. (6) in Ref. [12]) of our quasi-degenerate formulation [12].

Paldus and Čížek [38] used Green's function approach to obtain the explicit expressions for excitation energies. As they demonstrated in [30, 38] Green's function approach yields the same expressions for the excitation energies as does the time-independent MB-RSPT. They present the explicit formulae to the third order of perturbation expansion for the excitation energies. As is demonstrated in [13, 30, 38] the ionization potentials are implicitly included in excitation energies. This can be demonstrated also diagrammatically because our diagrams for ionization potentials in Fig. 1 represent the part of the selfenergy diagrams of the two-particle Green's function [30, 38]. To be more specific all our third order diagrams are simply the time-versions of the diagrams 12, 13 and 14 in [38]. There exists the one to one correspondence between the third order diagrams A1–A6, C1–C6 and D1–D6 from [10] and our diagrams 1–18 in Fig. 1. Our time-independent MB-RSPT approach to ionization potentials is the same as with time-independent R-S Green's function approach. Cederbaum's approach is the Green's function technique in the Brillouin-Wigner perturbative form.

What is commonly referred to as MB-RSPT is developed by occupation number representation, Wick's theorem and adiabatic approximation which are used to give the diagrammatic description of ordinary time-independent Rayleigh-Schrödinger perturbation theory. Brueckner [31] showed that the non-physical terms cancelled up to fourth order and the generalization to all orders was effected by Goldstone [32]. This is known as the linked cluster theorem which as a consequence provides the rules for drawing the diagrams. Using this formalism the whole problem of correctly obtaining the terms of the perturbation series is reduced to drawing a set of topologically distinct diagrams according to some rules. From each diagram we can write down the mathematical expression. The MB-RSPT is described in many textbooks (see e.g. Ref. [33]). Here we refer the reader to the excellent article by Paldus and Čížek [30] where for the first time the complete description of time-independent MB-RSPT is given.

Let us assume that a perturbed Hamiltonian of an atomic or molecular system may be written as

$$H = e_0 + H_0 + W \tag{2}$$

and the perturbed Schrödinger equation is

$$H|\Psi\rangle = E|\Psi\rangle \tag{3}$$

and e_0 is the scalar quantity, H_0 is an unperturbed Hamiltonian and W is a perturbation, $|\Psi\rangle$ is the exact wave function of the system. In the second quantization formalism these operators have the form

$$H_0 = \sum_A \varepsilon_A X_A^+ X_A \tag{4}$$

$$W = \frac{1}{2} \sum_{ABCD} \langle AB|v|CD\rangle X_A^+ X_B^+ X_D X_C - \sum_{AB} \langle A|g|B\rangle X_A^+ X_B$$

where X_A^+ and X_B are creation and annihilation operators defined on the orthonormal set of spinorbitals which are the solution of the one-particle eigenproblem $(h+g)|A\rangle = \varepsilon_A|A\rangle$. One of the basic concepts of MB-RSPT is a properly preselected non-degenerate "core" state vector [34]

$$|\Phi_0\rangle = \prod_{A\in FS} X_A^+|0\rangle \tag{5}$$

$$H_0|\Phi_0\rangle = E_0^{(0)}|\Phi_0\rangle; \qquad E_0^{(0)} = \sum_{A\in FS} \varepsilon_A \tag{6}$$

where the index A runs over all occupied orbitals taken from the Fermi sea one-particle functions, and $|0\rangle$ is the normalized vacuum state vector. Using the Wick theorem the Hamiltonian can be rewritten in the so called normal form

$$H=\langle\Phi_0|H|\Phi_0\rangle+\sum_{AB}\langle A|f|B\rangle N[X_A^+X_B] \\ +\frac{1}{2}\sum_{ABCD}\langle AB|v|CD\rangle N[X_A^+X_B^+X_DX_C] \tag{7}$$

where $\langle\Phi_0|H|\Phi_0\rangle$ is the scalar quantity representing the restricted HF ground state energy, f is the well known HF operator and $N[\cdots]$ is the normal product defined with respect to spinorbitals $\{|A\rangle, |B\rangle, \ldots\}$, $|\Phi_0\rangle$ is the HF Slater determinant for the ground state. Let us redefine our unperturbed and perturbed Hamiltonian in the following way

$$K_0=H_0-\langle\Phi_0|H_0|\Phi_0\rangle \tag{8}$$

$$K=H-\langle\Phi_0|H|\Phi_0\rangle \tag{9}$$

We have then for the perturbed and unperturbed eigenproblem, respectively

$$K|\Psi_i\rangle=k_i|\Psi_i\rangle \tag{10}$$

$$K_0|\Phi_i\rangle=\kappa_i|\Phi_i\rangle \tag{11}$$

The state $|\Phi_i\rangle$ is the initial state to $|\Psi_i\rangle$ and we assume that $|\Phi_i\rangle\to|\Psi_i\rangle$ if the perturbation is switched on. The perturbation expansion for the quantity k_i is given

$$k_i=\kappa_i+\sum_{n=0}^{\infty}\langle\Phi_i|W[Q_i(W+\kappa_i-k_i)]^n|\Phi_i\rangle \tag{12}$$

where

$$Q_i=\sum_{\substack{j\\(j\neq i)}}\frac{|\Phi_j\rangle\langle\Phi_j|}{\kappa_i-\kappa_j} \tag{13}$$

Let us study the ionized state which we shall describe by $|\Psi_0'\rangle$. Of course this will depend on the initial state of the neutral and charged system. Here we shall limit ourselves to such a state $|\Psi_0'\rangle$ for which the initial state $|\Phi_0'\rangle$ is obtained from the neutral closed-shell ground state in which we annihilate one particle. The corresponding eigenvalue problems are

$$K|\Psi_0'\rangle=k_i'|\Psi_0'\rangle \tag{14}$$

$$K_0|\Phi_0'\rangle=\kappa_i'|\Phi_0'\rangle \tag{15}$$

The state $|\Phi_0'\rangle$ we shall realize in the following way

$$|\Phi_0'\rangle=X_H|\Phi_0\rangle \tag{16}$$

The vertical ionization potential I_H is given by

$$I_H=k_0'-k_0 \tag{17}$$

In the present article we shall study the ionization potentials up to the third order of perturbation expansion. Therefore Eq. (17) can be rewritten using (12) in the form

$$\begin{aligned} I_H=&\langle\Phi'_0|K_0|\Phi'_0\rangle+\langle\Phi'_0|W|\Phi'_0\rangle+\langle\Phi'_0|WQ'_0W|\Phi'_0\rangle \\ &+\langle\Phi'_0|WQ'_0WQ'_0W|\Phi'_0\rangle-\langle\Phi_0|K_0|\Phi_0\rangle-\langle\Phi_0|W|\Phi_0\rangle \\ &-\langle\Phi_0|WQ_0W|\Phi_0\rangle-\langle\Phi_0|WQ_0WQ_0W|\Phi_0\rangle \end{aligned} \tag{18}$$

Since our Hamiltonian H (7) does not depend on the number of particles the Hamiltonian in (10) and (11) is the same as in (14) and (15). Using Eqs. (8) and (16) we can write Eq. (18) in the form

$$\begin{aligned} I_H=&\{\langle\Phi_0|X_H^+K_0X_H|\Phi_0\rangle+\langle\Phi_0|X_H^+WQ'_0WX_H|\Phi_0\rangle \\ &\langle\Phi_0|X_H^+WQ'_0WQ'_0WX_H|\Phi_0\rangle\}-\{\langle\Phi_0|WQ_0W|\Phi_0\rangle \\ &+\langle\Phi_0|WQ_0WQ_0W|\Phi_0\rangle\} \end{aligned} \tag{19}$$

The simplest separation of the Hamiltonian (7) to the form (2) i.e. to the unperturbed Hamiltonian and the perturbation is as follows

$$H_0=\sum_{A,B}\langle A|f|B\rangle N[X_A^+X_B] \tag{20}$$

$$W=\frac{1}{2}\sum_{A,B,C,D}\langle AB|v|CD\rangle N[X_A^+X_B^+X_DX_C] \tag{21}$$

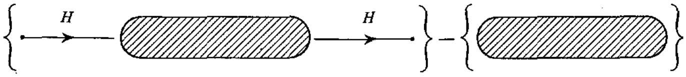
and the scalar quantity e_0 we identify with $\langle\Phi_0|\mathrm{H}|\Phi_0\rangle$. Let us assume that the spinorbitals $\{|A\rangle, |B\rangle\cdots\}$ are the eigenfunctions of the HF operator

$$f|A\rangle=\varepsilon_A|A\rangle \tag{22}$$

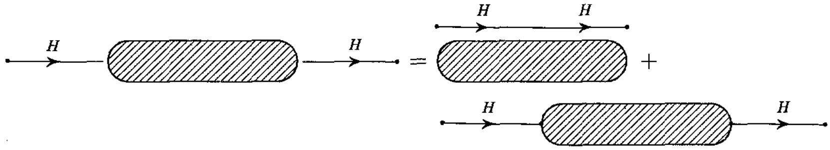
Then the unperturbed Hamiltonian has a diagonal form

$$H_0=\sum_A\varepsilon_AN[X_A^+X_A] \tag{23}$$

The individual terms of Eq. (19) can be calculated diagrammatically. The first term on the right hand side of (19) gives us $-\varepsilon_h$ which is well known Koopmans' theorem. Formally, we can write Eq. (19) in the following way

$I_H= -\varepsilon_h +$  (24)

The first term on the right hand side of (24) represents Koopmans' theorem, the second term represents the second and third terms from the right hand side of (19) and the third term of (24) represents the last two terms of (19). As was shown in [12] the second term of the right hand side of (24) which represents the correlation correction to ionized state can be decomposed into two parts, namely to the correlation correction to the parent state plus the remaining terms. We can formally represent this decomposition as

 (25)

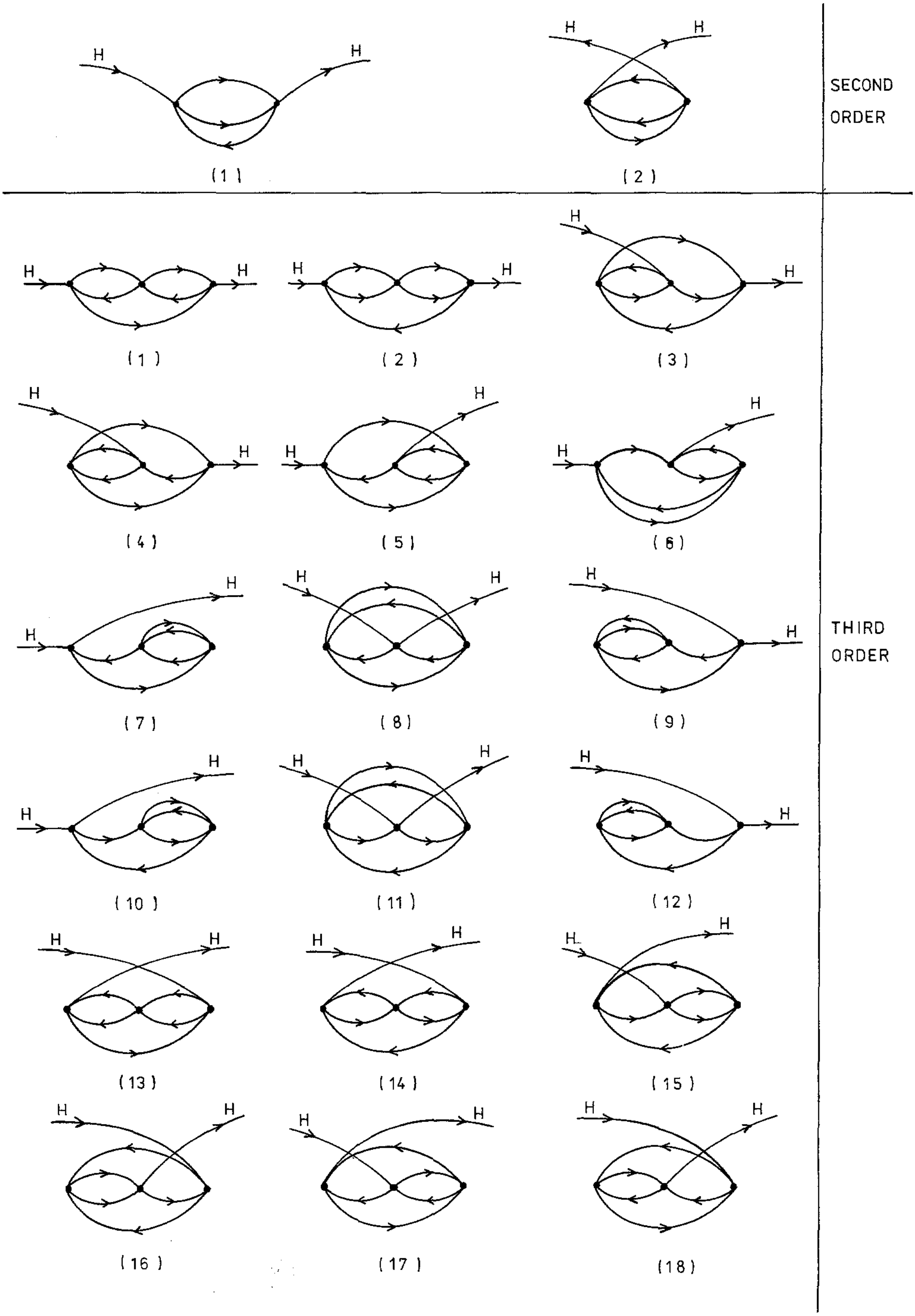
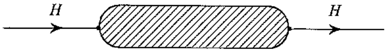


Fig. 1. The second and third order Hugenholtz's diagrams for vertical ionization potentials

where the first part on the right hand side of (25) is the correlation correction of the parent state and the second part is the remaining term. Due to this fact in Eq. (24) we can formally cancel those terms which contribute equally at least up to the third order of perturbation theory to the correlation correction of the ionized state and parent state. Eq. (24) can then be simply written as

$$I_H = -\varepsilon_H + \qquad (26)$$



The second term on the right hand side of Eq. (26) can be represented diagrammatically. In Fig. 1 we present the second and third order Hugenholtz's diagrams for this term from which explicit expression for Eq. (26) can be obtained.

3. Application to H_2O and Ne

We have applied the theory described in the previous part of this paper to the H_2O molecule and the Ne atom. We have selected these systems because excellent calculations were done by Cederbaum *et al.* [8, 9] using the Green's function technique on H_2O and Ne. The VIP's are defined as the difference between potential curves at the equilibrium geometry of the ground state. Therefore, to compare them with experiment they should be corrected for vibrational effects. The corrected experimental VIP's are taken from [25]. The SCF calculations were performed by Polyatom 2 program (QCPE 199). The wavefunction for H_2O was computed with a contracted Gaussian basis [$4s2p1d/2s1p$]. Exponents and contraction coefficients for oxygen were chosen according to Dunning [35] and that for hydrogen (unscaled) according to Huzinaga [36]. Exponents of polarization functions are the same as those used by Cederbaum *et al.*, $\alpha_d(\mathrm{O}) = 1.0$ and $\alpha_p(\mathrm{H}) = 0.75$ [8]. We have used essentially the experimental geometry, $R_{\mathrm{OH}} = 0.9572$ Å, $\measuredangle \mathrm{HOH} = 104.5$, the Cartesian coordinates H_1, H_2 $(0.0;\ \pm 1.430429;\ 1.107157)$ a.u. The energy, $E_{\mathrm{SCF}} = -75.042661$, is very close to the value given by Cederbaum *et al.* [8]. The differences in orbital energies are not larger than 0.01 eV. The results are shown in Table 1. The basis set for Ne atom is exactly the same as that used by Cederbaum and von Niessen [9]. It consisted of Cartesian Gaussian functions, 10 functions of s-type and 6 of p-type contracted to 5 functions of s-type and 3 of p-type. The exponential parameters and contraction coefficients are taken from [36]. The calculated SCF energy is $E_{\mathrm{SCF}} = -128.5312347$ a.u. The results of the calculation for Ne are given in Table 2. The contributions from individual diagrams for H_2O and Ne are presented in Table 3.

4. Discussion

To open the discussion we stress that our calculation of ionization potentials is a direct and not an iterative one. Let us compare the results for the H_2O molecule obtained by MB-RSPT with a Green's function calculation. We can see from Table 1 comparing A and B (in both cases 11 virtual MO's were taken into account) that the results performed by MB-RSPT are in nice agreement with the Green's function technique [8]. The significant difference is only for the $2a_1$ case for which the value given by MB-RSPT is about 0.65 eV closer to experiment than that given by Green's

Table 1. Vertical ionization potentials of H_2O[a]

State	Calculation[b]	Koopmans $-\varepsilon$	$\Delta\varepsilon^{(2)}$	$\Delta\varepsilon^{(3)}$	$\varepsilon^{(3)}$	Exper.[c] VIP	Exper.[c,d] cor.
$2a_1$	A	36.55	−3.62	2.17	35.10	32.2	
	B	36.56	−4.57	2.47	34.45		
	C	36.56	−4.87	1.98	33.66		
	D	37.07	−3.69	1.83	35.22		
$1b_2$	A	19.30	−1.60	1.52	19.22	18.55	18.72 ± 0.22
	B	19.29	−1.77	1.65	19.17		
	C	19.29	−1.49	1.39	19.19		
	D	19.53	−1.60	1.50	19.42		
$3a_1$	A	15.67	−2.49	2.00	15.18	14.73	14.83 ± 0.11
	B	15.66	−2.76	2.23	15.13		
	C	15.66	−2.46	1.91	15.12		
	D	15.44	−2.82	2.12	14.74		
$1b_1$	A	13.67	−2.75	2.11	13.03	12.61	12.78
	B	13.66	−3.12	2.37	12.91		
	C	13.66	−2.91	2.05	12.79		
	D	13.79	−3.31	2.27	12.75		

[a] Energies in eV, 1 a.u. = 27.21 eV. $\Delta\varepsilon^{(2)}$ and $\Delta\varepsilon^{(3)}$ are corrections to second and third order, respectively, of perturbation theory. $\varepsilon^{(3)}$ is the final value of VIP with second and third order corrections to Koopmans' theorem.

[b] Calculation A – results of Cederbaum *et al.* [8], using Green's functions. Basis [4*s*2*p*1*d*/2*s*1*p*]. Four highest occupied and eleven lowest unoccupied molecular orbitals were included. Calculation B – this work, with MB-RSPT. Basis [4*s*2*p*1*d*/2*s*1*p*]. Four highest occupied and eleven unoccupied molecular orbitals were included.

Calculation C – similar to the calculation B, but all 21 unoccupied molecular orbitals were included.

Calculation D – this work, with MB-RSPT. Basis [4*s*2*p*/2*s*], Ref. [35]. All occupied and all unoccupied molecular orbitals were included.

[c] Ref. [8].

[d] Ref. [25], ionization potentials, corrected for vibrational effects.

Table 2. Vertical ionization potentials in eV of Ne calculated with [5*s*3*p*] basis[a]

State	Calculation[b]	Koopmans $-\varepsilon$	$\Delta\varepsilon^{(2)}$	$\Delta\varepsilon^{(3)}$	$\varepsilon^{(3)}$	Exper. [9]
$1s$	A	891.67	−25.65			869.04
	B	891.88	−34.70	22.14	879.32	
$2s$	A	52.36	−4.09			48.47
	B	52.37	−4.50	3.19	51.06	
$2p$	A	23.13	−3.41	2.51	22.24	21.60
	B	23.14	−3.75	2.70	22.09	

[a] 1 a.u. = 27.21 eV. $\Delta\varepsilon^{(2)}$ and $\Delta\varepsilon^{(3)}$ are corrections to second and third order, respectively, of perturbation theory. $\varepsilon^{(3)}$ is the final value of VIP with second and third order corrections to Koopmans' theorem.

[b] Calculation A – results of Cederbaum and von Niessen [9]. Calculation B – our results. All occupied and all virtual molecular orbitals were included.

Table 3. Contributions to the VIP of H_2O and Ne from the individual diagrams. All virtual orbitals of H_2O are included (calculation C of Table 1). Energy values are given in a.u. (1 a.u. = 27.21 eV).

	H_2O				Ne
Diagram	$2a_1$	$1b_2$	$3a_1$	$1b_1$	$2p$
Sec. ord.					
1	−0.2122	−0.1134	−0.1457	−0.1594	−0.1760
2	0.0333	0.0586	0.0554	0.0523	0.0380
Third ord.					
1	−0.1740	−0.0406	−0.0542	−0.0617	−0.0550
2	0.1667	0.0488	0.0659	0.0744	0.0843
3 = 6	0.0563	0.0260	0.0395	0.0437	0.0433
4 = 5	0.0103	0.0081	0.0010	0.0111	0.0081
7 = 9	−0.0549	−0.0428	−0.0516	−0.0552	−0.0489
8	−0.0634	−0.0583	−0.0596	−0.0613	−0.0361
10 = 12	0.0663	0.0522	0.0616	0.0646	0.0700
11	0.0621	0.0546	0.0567	0.0589	0.0365
13	−0.0055	−0.0123	−0.0106	−0.0089	−0.0052
14	0.0064	0.0130	0.0115	0.0097	0.0052
15 = 16	−0.0123	−0.0220	−0.0209	−0.0199	−0.0130
17 = 18	0.0146	0.0245	0.0221	0.0200	0.0101

functions. Here we have to mention that in [8] only the poles of Green's function which are situated far from the poles of the self-energy part, i.e. which belong to the interval $(\Sigma_{-1}, \Sigma_{+1})$ are investigated. For the case $2a_1$ this condition is not satisfied. As is mentioned in [8] these results can be improved considering all the virtual orbitals. For numerical reasons Cederbaum *et al.* [8] did not take into account all virtual orbitals. In our calculations we have included all 21 virtual orbitals. The results show (calculation C in Table 1) that the inclusion of all virtual orbitals influenced significantly only $2a_1$ state. This state is shifted by 0.8 eV closer to experiment. The effect on other states is negligible. This concerns only the total value of VIP's. The contributions to second and third order of perturbation theory taken separately are influenced more by the inclusion of all the virtual orbitals but there is a compensation effect ($\Delta\varepsilon^{(2)}$ and $\Delta\varepsilon^{(3)}$ are of different sign). All the other conclusions are identical with those of Cederbaum *et al.* [8]. The inclusion of the second order of perturbation expansion is insufficient, it leads to overestimation of the correction. In some cases it gives even worse agreement with experiment than Koopmans' theorem. Inclusion of third order has a compensation effect and gives good agreement with experiment. For the sake of completeness we present also the calculations with double zeta basis (results D in Table 1). We see that for the H_2O molecule the effect of the basis is small at least for the first three VIP's which is the same as in [22]. The agreement with experiment is good. Here we have to stress that we have compared only the calculations up to third orders of both theories. Cederbaum *et al.* [8] did some infinite summation of some preselected diagrams which significantly improved the results. This can be done also in MB-RSPT and we want to do this in our forthcoming paper. For completeness we present in Table 3 the individual contributions from different diagrams.

In their calculation of the Ne atom Cederbaum and von Niessen [9] have included all 9 virtual orbitals to calculate the corrections to $2p$ Koopmans' ionization potential up to third order. Corrections to $1s$ and $2s$ Koopmans' ionization potentials were calculated up to second order with some infinite summations. In Table 2 we present our calculations up to third order of MB-RSPT as compared to the work [9]. The results show good agreement with experiment for the $2p$ VIP. The others VIP's are not in such a good agreement with experiment. This is of course understandable because the $[5s3p]$ basis does not include the orbitals with a higher angular momentum. Due to this fact any comparison with experiment is meaningless. We can say that MB-RSPT improves Koopmans' VIP's in a correct way. For the $2p$ VIP the results using Green's functions and MB-RSPT are essentially equivalent in the second plus third order. However, in the second and third orders, taken separately the differences between both calculations are rather large. To a lesser extent, this is found also in calculations of H_2O. The similar effect of diagrammatic cancellation as in Green's function technique exists for the Ne atom as for the H_2O molecule as can be seen from Table 3.

Here we would like to make still a few comments to other methods which are used to calculate VIP's. The approach developed by Simons *et al.* [15–18] is based on the equation of motion method. They have developed the formulae for the electron affinities and ionization potentials calculations through third order in the electronic interaction. Simons *et al.* define the operator Ω (Eq. (2) in Ref. [18]) which generates in principle the exact eigenstate $|\Psi'\rangle$ of the positive ion when operating on the true neutral molecular ground state $|\Psi\rangle$. The operator Ω is defined in terms of creation and annihilation operators and the wave function of the ground state $|\Psi\rangle$ of the parent system is chosen using the Rayleigh-Schrödinger perturbation expansion. Due to this there exists close connection of this method with the Green's function approach and that based on MB-RSPT. Namely the form of the operator Ω is responsible for the fact that comparing the third orders of the equation of motion method and of MB-RSPT, we see that the third order of equation of motion method corresponds to infinite summation of some preselected diagrams which appear in MB-RSPT. To understand the connections of the equation of motion method with MB-RSPT to all orders the detailed analysis of the form of operator Ω must be done. This problem is partly discussed in [37].

Chong *et al.* [21, 22] used the third order ordinary Rayleigh-Schrödinger perturbation theory to calculate VIP's. The ionization potential is calculated as a difference in the energy expectation values of the ionized and parent systems. In this approach we have to take care whether the wavefunction of the parent and ionized systems are of the same quality. Moreover, the advantage of MB-RSPT is also in the fact that we can use the effect of formal cancellation of those terms which contribute equally to the correlation energy of the parent and ionized systems to obtain the explicit formula for VIP's. To compare these two methods we have performed calculations of VIP's for the H_2O molecule in double-zeta basis. The results are presented in Table 1 (results D).

As we have already said the diagrammatic approach gives us the "microscopic view" on the theory and we can see which diagrammatic contributions are dominant. We can try then to sum these contributions up to all orders of perturbation theory. This we shall try to do in our next paper.

Acknowledgement. The calculations were carried out on the Siemens 4004 at the Computer Centre of Komenský University in Bratislava. The computer time is gratefully acknowledged.

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Received November 18, 1976/February 24, 1977