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Application of One-Particle Green Functions Technique for Calculation of Vertical Ionization Potentials of Closed-Shell Molecules Described by CNDO/2 Semiempirical Hamiltonian

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A simple method of infinite summations of some dominant diagrams in the framework of the one-particle Green functions technique is suggested. This method for the calculation of the low-lying vertical ionization potentials of some simple closed-shell molecules described by CNDO/2 semiempirical Hamiltonian is applied. The obtained results are in quite-satisfactory agreement with the experimental values of the vertical ionization potentials measured by the photo-electron spectroscopy technique.

Key words: Vertical ionization potentials – Green functions

1. Introduction

An up-to-date development of quantum chemical methods for calculation of the vertical ionization potentials (VIP) of molecules has been mainly stimulated by the recent experimental possibilities of precise measuring of the VIP's (photo-electron spectroscopy, ESCA; cf. for example Refs. [1, 2]). Applications of the well-known Koopmans' theorem [3] for the calculation of the low-lying VIP's (and also for interpretation of the photo-electron spectra) are limited merely to a special class of molecules, where the correlation and rearrangement effects are negligible or mutually compensated. Furthermore, as has been recently observed by Hohlneicher *et al.* [4], there exists complete breakdown of Koopmans' theorem for some small molecules, when a distance between two neighbouring VIP's is very small with respect to their absolute values. Therefore we may conclude from these introductory remarks concerning the applicability of Koopmans' theorem that a quite satisfactory theory for the calculation of the low-lying VIP's should take into account, in any form, the above mentioned correlation as well as rearrangement effects. These effects can be included in theory by two different ways:

Firstly, by the configuration interaction method, where separate calculations for the neutral and the singly ionized molecule should be carried out. Then, the low-lying VIP's are approximated as a difference between ground-state energy of the neutral molecule and either ground-state (for the first VIP) or excited (for the higher VIP) energies of the singly ionized molecule. Unfortunately, this simple approach has one serious drawback among others, namely, the calculated VIP's are equal to the difference of two large quantities, which requires a high accuracy of the calculated energies.

Secondly, by the diagrammatic degenerate (or quasi-degenerate) perturbation theory. In this theoretical approach VIP's are determined directly as eigenvalues of a finite-dimensional model eigenproblem. It can be divided into three methods, (1) diagrammatic (quasi-) degenerate Rayleigh-Schrödinger perturbation theory [5, 6], (2) Bloch-Horowitz perturbation theory [7, 8], and (3) one-particle Green functions technique [4, 9–13]. All these methods for the direct calculation of VIP's yield, in principle, their exact theoretical values in the framework of the given *ab initio* and semiempirical Hamiltonian, respectively.

The scope of the present communication is the application of the one-particle Green functions technique for the direct calculations of the low-lying VIP's of closed shell molecules described by the semiempirical CNDO/2 Hamiltonian. Similarly as in the *ab initio* Hamiltonian [4], we have observed that for a good agreement of the calculated VIP's with experimental ones, some higher than the second order diagrammatic contributions should be taken into account. To overcome this difficulty, Hohlneicher *et al.* [4, 13] included all second and third order diagrams, and furthermore these diagrammatic contribution have been completed by infinite summations of some preselected (assumed to be dominant) diagrams. Thus, they obtained a quite satisfactory perturbation diagrammatic "powerful machinery" for the theoretical prediction of low-lying VIP's. We stress that all these theoretical conclusions are made for the *ab initio* Hamiltonian constructed by Gaussian atomic orbitals. Recently, the same approach was applied by Kellerer *et al.* [14] also for the semiempirical CNDO/2 Hamiltonian. They started from the *ab initio* Hartree-Fock orbital energies (Koopmans' theorem is used as a zeroth order approximation) and correlation and rearrangement corrections are calculated by using the two-particle repulsion molecular integrals resulting from CNDO/2 method. We are afraid that such clumsy mixture of the *ab initio* and semiempirical method is, at least, inconsistent. We show that this inconsistency may be simply removed, when the whole one-particle Green functions technique is completely realized in the framework of CNDO/2 semiempirical Hamiltonian. I.e., the Hartree-Fock orbital energies as well as the two-particle integrals are taken in calculations exclusively from CNDO/2 method. Furthermore, as it follows from our numerical results obtained for some small closed-shell molecules (H_2O, CO, N_2, F_2, H_2CO and HF), the third order diagrammatic contributions may be omitted when the infinite summations of preselected dominant diagrams are used. Of course, these observations are true, probably, when the semiempirical CNDO/2 Hamiltonian is used in the above consistent way.

Let us now interrupt our introductory remarks and turn our attention to some very interesting conclusions which follow from the above-discussed observations, that for a good agreement of the calculated VIP's with experimental ones, at least, some higher order diagrammatic contributions should be taken into account. A similar situation, and probably even worse one, exists also for the direct calculations of the low-lying excitation energies by the two-particle Green functions technique [15, 16]. A usual way to remove this drawback of the Hartree-Fock orbitals is based on the concept of the "new" renormalized one- and/or two-particle interactions, well-known method in the up-to-date microscopic theory of nuclei [17, 18]. The above mentioned infinite summations of some pertinent diagrams may be understood as a rudimentary realization of this concept. Unfortunately, a correct theoretical treatment of the renormalized interactions for finite non-homogeneous N-electron systems is quite complex problem and contains many unresolved theoretical and computational pitfalls.

Recently, we have suggested [19] a promising solution of this problem that the Hartree-Fock orbitals do not form a best frame for the direct diagrammatic-perturbation calculations of VIP's and excitation energies. In this connection we have focused our interest to another type of the one-particle orbitals, namely, to the Brueckner orbitals and generalized natural orbitals, which are involving some part of the correlation effects on the one-particle level. This possibility is very closely related to the technique of the renormalized interactions, as has been shown in the recent works concerning the microscopic theory of nuclei [20–22].

To conclude this Introduction we emphasize that although we believe that a near future of quantum chemistry will be given by the *ab initio* methods, now, the suggested diagrammatic-perturbation method using the semiempirical CNDO/2 Hamiltonian may serve as a very simple and efficient tool predicting the low-lying VIP's.

2. Theory

The one-particle Green function $G_{ab}(t)$ in the Heisenberg picture is defined as follows [23, 24]

$$G_{ab}(t) = -i \langle \Psi_0^N | T[X_a^+(t)\, X_b(t'=0)] | \Psi_0^N \rangle \,, \tag{1}$$

where $|\Psi_0^N\rangle$ is the normalized exact ground-state vector of an N-electron molecular system, $X_a^+(t)$ and $X_b(t)$ are creation and annihilation operators in the Heisenberg picture defined with respect to the orthonormal set of Hartree-Fock spinorbitals, and finally the symbol $T[\ldots]$ is the Wick chronological product. The thus defined one-particle Green function can be transformed into ω-representation by using the Fourier transformation,

$$G_{ab}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t}\, G_{ab}(t)\, dt \,. \tag{2}$$

Then, as one may observe from simple theoretical considerations, negative poles of $G_{ab}(\omega)$ are equivalent directly to the VIP's of the given N-electron molecular system. To realize this possibility we use the Dyson equation [23, 24] expressing a connection between the Green function (2) and its so called self-energy part,

$$G^{-1}(\omega) = \omega I - \mathscr{E} - M(\omega), \tag{3}$$

where for the sake of simplicity we have used a matrix notation, $\mathscr{E}$ is a diagonal matrix with Hartree-Fock orbital energies, and I is a unity matrix. The matrix-valued function $M(\omega)$ is the self-energy part of the Green function $G(\omega)$, and may be expressed in the diagrammatic-perturbation treatment as a sum of all pertinent diagrams without external lines, i.e. it can be written as a perturbation expansion

$$M(\omega) = \sum_{\nu=1}^{\infty} M^{(\nu)}(\omega), \tag{4}$$

here $M^{(\nu)}(\omega)$ is the sum of all possible contributions of the νth order. For the canonical [25] Hartree-Fock spinorbitals, the first order contributions to $M(\omega)$ are identically equal to zero, $M^{(1)}(\omega) = 0$. This means that Koopmans' theorem is true up to the first order. As has been mentioned above, the negative poles of $G(\omega)$ are equivalent to the VIP's, therefore solving the following pseudo-eigenvalue problem

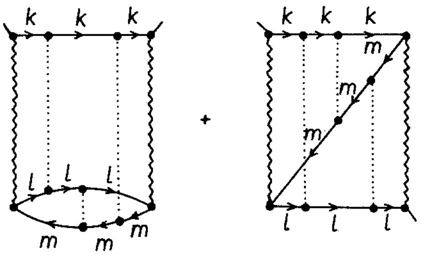
$$\omega I - [\mathscr{E} + M(\omega)] = 0, \tag{5}$$

we obtain directly VIP's determined coherently with above mentioned note as an eigenvalue of this problem.

Recently, Hohlneicher and Cederbaum [12] have used this method when the self-energy part is expressed up to the second order, i.e. $M(\omega) = M^{(2)}(\omega)$ [remember that $M^{(1)}(\omega) = 0$], and the total Hamiltonian of a given molecular system is approximated by an *ab initio* Hamiltonian constructed from Gaussian atomic orbitals. They have obtained for the formaldehyde molecule results which nicely agree with experimental values for the low-lying VIP's. Unfortunately, this good agreement has not been generally observed for others simple molecules [4]. Then, Hohlneicher *et al.* [4, 13] have summarized from their calculations with above-mentioned *ab initio* Hamiltonian, that for a good agreement of the calculated VIP's with experimental ones, the third order diagrammatic contributions and some special infinite summation should be added to the second order diagrammatic contributions to the self-energy part.

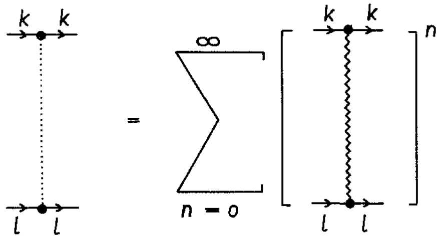
In the present communication we have adapted this conclusion for CNDO/2 Hamiltonian by the following way. Firstly, we take into account all possible the second order diagrammatic contributions. Secondly, the third and higher order diagrammatic contributions are approximated by the infinite summation of some dominant diagrams. This infinite summation has been determined by a maximal appearing of the Coulomb two-particle molecular integrals simultaneously with saving of a simplicity of the final expression. This procedure is supported by actual numerical values of the two-particle molecular integrals by CNDO/2 semi-empirical scheme. These numerical values, taken from the calculation of the H_2O molecule, of the Coulomb integrals are about 0.6–0.7 a.u. in contrast to the fact that all possible remaining integrals have absolute values, at least, about one order lower than previous ones. Then, the self-energy part $M(\omega)$ can be approximated by the following diagrammatic expression

$M(\omega) =$



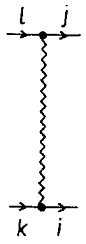
(6)

The dotted two-particle vertices represent the infinite summation of the original (waved) two-particle vertices



(7)

where



$$= <ij/kl> \tag{8}$$

Application of rules of the Goldstone graphology (cf. for example Refs. [13, 24]) to the diagrammatic expression (6–7) gives

$$\begin{aligned} M_{ij}(\omega) = \sum_{k,l,m}^{*} \Bigg\{ & \frac{\langle kl|mi\rangle\,(2\langle mj|kl\rangle - \langle mj|lk\rangle)}{W_{klm}(\omega)} \\ & \times \sum_{r=0}^{\infty} \left[\frac{\langle kl|kl\rangle\,(-1)^{1+\nu(m)}}{W_{klm}(\omega)} \right]^{r} \\ & \times \sum_{s=0}^{\infty} \left[\frac{\langle lm|lm\rangle\,(-1)^{\nu(m)}}{W_{klm}(\omega)} \right]^{s} \\ & \times \sum_{t=0}^{\infty} \left[\frac{\langle km|km\rangle\,(-1)^{\nu(m)}}{W_{klm}(\omega)} \right]^{t} \Bigg\}, \end{aligned} \tag{9}$$

where the starred summation should be read as

$$\sum_{k,l,m}^{*} = \sum_{k,l \in \{\mathrm{occ}\}} \; \sum_{m \notin \{\mathrm{occ}\}} + \sum_{k,l \notin \{\mathrm{occ}\}} \; \sum_{m \in \{\mathrm{occ}\}}, \tag{10}$$

$\{\mathrm{occ}\}$ being the set of the occupied spinorbitals and the integer-valued function $v(m)$ is defined as follows

$$v(m) = \begin{cases} 0 & \text{for} \quad m \notin \{\mathrm{occ}\} \\ 1 & \text{for} \quad m \in \{\mathrm{occ}\} \end{cases} \tag{11}$$

Finally, the function $W_{klm}(\omega)$ from the denominators in (9) is determined by

$$W_{klm}(\omega) = \omega + \varepsilon_m - \varepsilon_k - \varepsilon_l\,, \tag{12}$$

here ε_m, ε_k, and ε_l are the Hartree-Fock orbital energies. After simple algebraic manipulations and summing up the spin parts (keeping in mind that we have consider a closed-shell molecular system) from the two-particle integrals, the expression (9) can be written in the final simple form

$$\begin{aligned} M_{ij}(\omega) = \sum_{k,l,m}{}^{*} \Bigg[& \frac{\langle kl|mi\rangle\,(2\langle mj|kl\rangle - \langle mj|lk\rangle)}{W_{klm}(\omega)} \\ & \times \frac{W_{klm}(\omega)}{W_{klm}(\omega) - \langle kl|kl\rangle\,(-1)^{1+v(m)}} \\ & \times \frac{W_{klm}(\omega)}{W_{klm}(\omega) - \langle lm|lm\rangle\,(-1)^{v(m)}} \\ & \times \frac{W_{klm}(\omega)}{W_{klm}(\omega) - \langle km|km\rangle\,(-1)^{v(m)}} \Bigg], \end{aligned} \tag{13}$$

where only spatial molecular orbitals occur. To summarize this theoretical Section, starting from the detailed inspection concerning the numerical values of the two-particle integrals from CNDO/2 Hamiltonian, we have suggested a simple tractable approximate formula (13) for the matrix elements of the self-energy part. This formula contains complete second-order diagrammatic contributions simultaneously with higher-order contributions approximated by the above introduced infinite summations.

3. Applications and Discussion

For a numerical illustration of the suggested approximate procedure for the construction of the self-energy part matrix, we have carried out calculation of VIP's of some small closed-shell molecules (H_2O, CO, N_2, F_2, H_2CO, and HF). Although almost all these molecules have been studied [26] by a similar approach in the framework of the *ab initio* Hamiltonian, the scope of the present illustrative applications is to verify an applicability of CNDO/2 semiempirical scheme for the calculation of VIP's by our proposed approximate diagrammatic-perturbation method. We emphasize that we have used CNDO/2 Hamiltonian therefore, since this semiempirical method applied to small molecules is very "closely related" to the *ab initio* calculations [27]. This means that overcounting of the correlation effects may be neglected in the Hartree-Fock calculations with CNDO/2 semiempirical parametrization. We know that similar considerations

Table 1. Results for H_2O molecule[a] (I^{exp} – experimental value of VIP; $I^{(0)}$ – VIP according to Koopmans; $I^{(2)}$ – VIP using self-energy part up to second order; $I^{(\infty)}$ – VIP using the infinite summation of dominant diagrams)

Symmetry MO	I^{exp}, eV[b]	$I^{(0)}$, eV	$I^{(2)}$, eV	$I^{(\infty)}$, eV
$1b_2$	18.72 ± 0.22	21.00	20.57	19.60
$2a_1$	14.83 ± 0.11	19.20	17.76	15.96
$1b_1$	12.78	17.81	15.41	12.75

[a] Calculations were carried out with experimental geometry [29].
[b] Ref. [30].

about overcounting of the correlation effects in the semiempirical Hartree-Fock calculations are very problematic, but nevertheless they might be of value, at least, for the naïve orientation in this given complex problem. Thus for example, Dewar's [28] semiempirical MINDO/2 scheme is not applicable for our purpose, because its parametrization was selected in such a way, that among others, the Hartree-Fock orbital energies (for some class of molecules) more or less estimate the low-lying VIP's. This observation can be explained by the following two alternative ways: (1) it is true only for the given carefully selected class of molecules, or (2) the correlation effects are taken into account in the framework of the Hartree-Fock method by a proper selected parametrization.

The numerical values of the first three low-lying VIP's of H_2O molecule calculated by our proposed diagrammatic method are presented in Table 1 (cf. also Fig. 1). In Table 2 the first VIP's of some small closed-shell molecules are presented only, because during the solution of the pseudo-eigenvalue problem (5) the convergence difficulties appear. In some case (namely for higher VIP's) Koopmans' theorem is not a proper starting step in our linear simple iterative

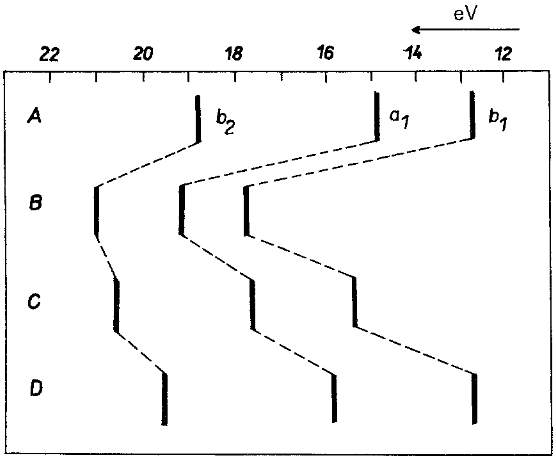


Fig. 1. Experimental [30] and calculated vertical ionization potentials of H_2O (A – experimental value of VIP; B – VIP according to Koopmans; C – VIP using self energy part up to second order; D – VIP using the infinite summation of dominant diagrams)

Table 2. The first VIP's of studied molecules[a] (The abbreviations are explained in Table 1)

Molecule	Symmetry MO	I^{exp}, eV	$I^{(0)}$, eV	$I^{(2)}$, eV	$I^{(\infty)}$, eV
H_2CO	b_2	10.88[b]	14.53	12.35	10.48
N_2	σ_g	15.60[b]	18.29	17.19	15.94
HF	π	16.06[c]	20.11	18.49	16.31
CO	σ	14.00[d]	17.26	16.48	15.73
F_2	π_g	15.63[c]	22.09	18.53	14.20

[a] Calculations were carried out with experimental geometry [29].
[b] Ref. [1].
[c] Ref. [31].
[d] Ref. [32].

procedure [schematically expressed by the scheme: $X_{k+1} = f(X_k)$] which was used for the solution of (5).

In contrast to the papers of Hohlneicher *et al.* [4, 26], in our case the perturbation contributions are of same sign, i.e., the calculated VIP's monotonically tend to the experimental values. Also the similar behaviour has been observed, when VIP's were calculated by the diagrammatic (quasi-) degenerate Rayleigh-Schrödinger perturbation theory with CNDO/2 Hamiltonian [33]. Therefore, we hope that this specific behaviour, observed in our work for the perturbation contributions to VIP's may be explained by the fact that a CNDO/2 semiempirical Hamiltonian was used.

We believe that from these simple illustrative calculations it follows that the suggested theory realized by the help of a CNDO/2 semiempirical Hamiltonian forms a very simple and efficient tool for predicting the low-lying VIP's.

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