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The CNDO Approximation in the Green's Function Method for VIP Calculation

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By introducing a CNDO adapted approximation into an appropriate irreducible interaction part a simple formula for calculation of vertical ionization potentials (VIP's) is derived. The method is applied to the molecules F_2, HF, C_2F_4, CH_2F_2, BF_3, CH_3F, CF_4.

Key words: Green's functions – VIP Calculation

1. Introduction

The first connection of the Green's function method for VIP calculation with the CNDO approximation was made by Kellerer *et al.* [1, 2] who inserted CNDO values into formulas for Koopmans' defects used earlier by Cederbaum *et al.* [3–6] with *ab initio* values. The Koopmans' defects obtained in this way were added to *ab initio* orbital energies. Biskupič *et al.* [7], however, argued that defects calculated with CNDO data should be added to CNDO orbital energies and tried to take account of the specific CNDO properties by an adequate approximation for the irreducible self-energy part in the Dyson equation. This latter approach is not expected to yield as reliable results as one based on *ab initio* calculations. On the other hand, because of the difficulty to perform *ab initio* calculations for larger molecules, it should be useful to have a method which is completely within the CNDO framework. In Ref. [7] the approximation for the irreducible self-energy part was determined by a maximal appearing of Coulomb two-particle molecular integrals (which were numerically found to be dominant against the others) simultaneously with saving of a simplicity of the final expression, but as mentioned by Lazzeretti *et al.* [18] this self-energy part has wrong analytical properties. Moreover, the construction of the self-energy part in Ref. [7] seems to be rather intuitive.

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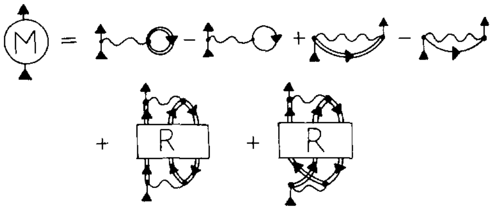
The purpose of our paper is, therefore, to extend this attempt by giving an alternative approximation for the irreducible self-energy part with correct analytical properties, found in a deductive manner.

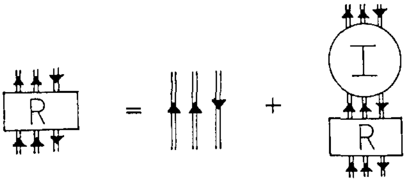
2. Theory

Using the Goldstone diagram-technique, the rules for which are listed e.g. in Ref. [8], p. 65 (we draw only one time-ordering for all), the exact irreducible self-energy part *M* can be written as definition for a response function *R* [9, 10]:



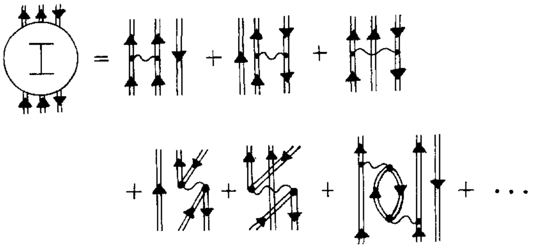
(1)

By stating a Dyson-like equation for *R* one can define an irreducible interaction part I [9, 10]:



(2)

(The irreducibility of I means that it is not possible to split I by merely cutting one triplet of parallel lines.) The diagrammatic expansion of I starts with:



(3)

We enter now the CNDO framework [11, 1, 2, 7], i.e. we take CNDO values for the Hartree–Fock orbital energies ε_i and evaluate the molecular matrix elements V_{ijkl} by

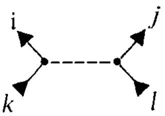
$$V_{ijkl} = \sum_{\mathrm{A,B}} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} c_{\mu i} c_{\mu k} c_{\nu j} c_{\nu l} \gamma_{\mathrm{AB}} \tag{4}$$

where γ_{AB} are the CNDO Coulomb two-particle atomic integrals and $c_{\mu i}$ the CNDO coefficients.

In this framework we make the following approximations:

A. We disregard renormalization, i.e. we replace in Eqs. (1)–(3) all double lines by single ones.

B. We introduce a CNDO adapted interaction into the irreducible interaction part, i.e. we replace all wiggled lines in I by dashed ones which are to be read as:



contributes a factor $\gamma\delta_{ik}\delta_{jl}$

where γ is an average of the occurring γ_{AB}:

$$\gamma = \frac{\sum_{\mathrm{A,B}} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} \gamma_{\mathrm{AB}}}{\sum_{\mathrm{A,B}} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} 1}$$

C. We assume M to be nearly diagonal, i.e., we set:

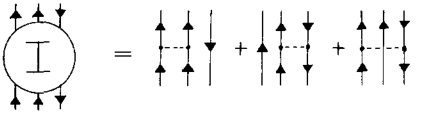
$$M_{ij}(\omega) \approx M_{ii}(\omega)\delta_{ij}$$

Approximation *A* permits confining to low lying VIP's, which is advisable, since the final iteration procedure converges slowly for higher VIP's. Approximation *B* is obtained by replacing in (4) all the γ_{AB} by the mean value γ (which is an approximation invariant to all AO-transformations [11]) and employing the orthogonality of the CNDO coefficients matrix $c_{\mu i}$ [11]:

$$V_{ijkl} \approx \gamma \sum_{\mu} c_{\mu i} c_{\mu k} \sum_{\nu} c_{\nu j} c_{\nu l} = \gamma\delta_{ik}\delta_{jl} \tag{5}$$

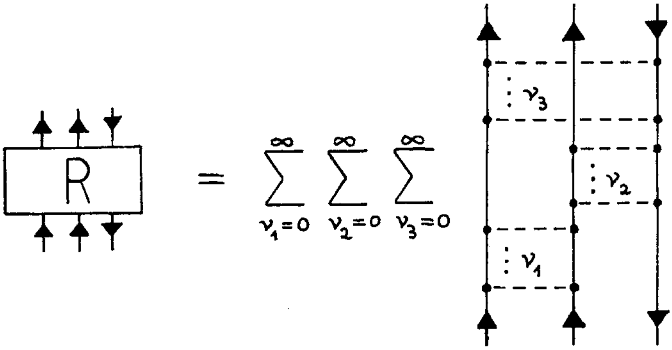
Approximation *C* is encountered even in the *ab initio* framework [5, 6] and should also be allowed in the cruder CNDO framework [1, 2, 18].

With these approximations Eq. (3) becomes:



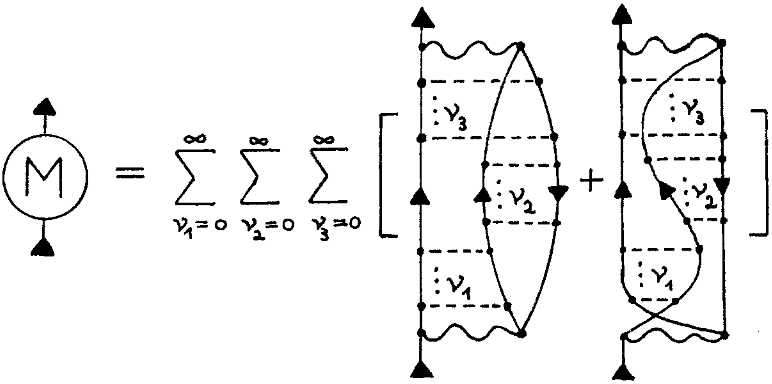
(6)

The expansion now terminates after the third term. This is because in all further diagrams we find that a particle and a hole line meet at the same end of a dashed line, which makes the diagram vanish (the dashed line yields a δ_{ik}, while i and k run over different index sets). Inserting (6) into (2) (with approximation A) we get:



(7)

(The dots symbolize that there are ν_1, ν_2, ν_3 equal dashed lines.) Going on to the irreducible self-energy part (1) (observing approximation A) we have:



(8)

For translating these diagrams we have to first perform the time permutations. Noting again that all diagrams with parts as  or  vanish, only the time orderings remain for which the dashed lines are situated between the wiggled lines. Furthermore, diagrams which are distinguished merely by a permutation of dashed lines give equal values (there are $[(\nu_1 + \nu_2 + \nu_3)!/\nu_1!\, \nu_2!\, \nu_2!]$ such diagrams for given ν_1, ν_2, ν_3). In this way we obtain:

$$
\begin{aligned}
M_{ij}(\omega) = {} & \sum_{\nu_1=0}^{\infty} \sum_{\nu_2=0}^{\infty} \sum_{\nu_3=0}^{\infty} \frac{(\nu_1+\nu_2+\nu_3)!}{\nu_1!\,\nu_2!\,\nu_3!} \\
& \cdot \Bigg[\sum_{\substack{m\in \mathrm{occ} \\ k,l\notin \mathrm{occ}}} \frac{V_{imkl}(V_{kljm}-V_{klmj})}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l} \cdot \left(\frac{\gamma}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l}\right)^{\nu_1} \\
& \cdot \left(\frac{-\gamma}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l}\right)^{\nu_2} \cdot \left(\frac{-\gamma}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l}\right)^{\nu_3} \\
& + \sum_{\substack{m\notin \mathrm{occ} \\ k,l\in \mathrm{occ}}} \frac{V_{imkl}(V_{kljm}-V_{klmj})}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l} \cdot \left(\frac{-\gamma}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l}\right)^{\nu_1} \\
& \cdot \left(\frac{\gamma}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l}\right)^{\nu_2} \cdot \left(\frac{\gamma}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l}\right)^{\nu_3} \Bigg]. \qquad (9)
\end{aligned}
$$

(occ is an abbreviation for the index set of occupied spin orbitals.) Using the multinomial theorem we can convert the three ν-summations into one and sum up the resulting geometrical series, thus ending with:

$$
\begin{aligned}
M_{ij}(\omega) = {} & \sum_{\substack{m\in \mathrm{occ} \\ k,l\notin \mathrm{occ}}} \frac{V_{imkl}(V_{kljm}-V_{klmj})}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l+\gamma} \\
& + \sum_{\substack{m\notin \mathrm{occ} \\ k,l\in \mathrm{occ}}} \frac{V_{imkl}(V_{kljm}-V_{klmj})}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l-\gamma}. \qquad (10)
\end{aligned}
$$

We mention that our M conserves the analytical properties of the exact irreducible self-energy part as described in Ref. [19]. Furthermore, it is interesting to note that (10) is closely related to Eq. (4.31) of Ref. [10] which was used with *ab initio* values: we obtain (10) if we set $V_{ijkl} \to \gamma\delta_{ik}\delta_{jl}$ in the denominator of Eq. (4.31) of Ref. [10]. From this connection it might be plausible to take some effective γ_i for different orbitals φ_i. Another possible modification would be to treat γ as a parameter and determine it through numerical fitting. However, these further modifications will not be considered here.

Let us now proceed to the VIP calculation. The negative VIP's, occurring as poles of the one-particle Green's function, are obtained as zeros of the eigenvalues of the inversed Green's function matrix G^{-1} which is given by the inverse Dyson equation (cf. e.g. Ref. [8], p. 64):

$$[G^{-1}(\omega)]_{ij} = (\omega - \varepsilon_i)\delta_{ij} - M_{ij}(\omega). \qquad (11)$$

By means of approximation C the matrix G^{-1} becomes diagonal and therefore the negative VIP's, denoted by ω_i, are determined by:

$$\omega_i = \varepsilon_i + M_{ii}(\omega_i). \qquad (12)$$

This is solved by iteration:

$$\omega_i = \lim_{N\to\infty} \omega_i^{(N)}$$

with

$$\begin{aligned}\omega_i^{(0)} &= \varepsilon_i\\ \omega_i^{(N+1)} &= \varepsilon_i + M_{ii}(\omega_i^{(N)})\\ &= \varepsilon_i + \sum_{\substack{m\in\mathrm{occ}\\ k,l\notin\mathrm{occ}}} \frac{V_{imkl}(V_{imkl} - V_{imlk})}{\omega_i^{(N)} + \varepsilon_m - \varepsilon_k - \varepsilon_l + \gamma}\\ &\quad + \sum_{\substack{m\notin\mathrm{occ}\\ k,l\in\mathrm{occ}}} \frac{V_{imkl}(V_{imkl} - V_{imlk})}{\omega_i^{(N)} + \varepsilon_m - \varepsilon_k - \varepsilon_l - \gamma}.\end{aligned} \tag{13}$$

In case of closed-shell molecules we can perform the spin summations which corresponds to replacing the numerators in (13) by $V_{imkl}(2V_{imkl} - V_{imlk})$ – all the indices designating only spatial orbitals then.

3. Applications

To test the above described method, we applied it to some closed-shell molecules. Kellerer *et al.* [1, 2] mentioned that symmetry may cause fortuitous results in the CNDO framework. We tried to avoid this influence by selecting molecules from different symmetry groups, namely $F_2(D_{\infty h})$, $HF(C_{\infty v})$, $C_2F_4(D_{2h})$, $CH_2F_2(C_{2v})$, $BF_3(D_{3h})$, $CH_3F(C_{3v})$ and $CF_4(T_d)$.

The results of our calculations are reported in Tables 1–7. We explain now the quantities listed there: $I^{(0)}$ are the VIP's according to Koopmans' theorem, i.e. the CNDO orbital energies with reversed sign, which were calculated by a CNDO/2 library program [15] using the following geometries [16]: (F_2) F–F = 1.4177 Å; (HF) H–F = 0.917 Å; (C_2F_4) C–C = 1.27 Å, C–F = 1.33 Å, ∢FCF = 110°;

Table 1. VIP's for F_2 (in eV), $\gamma = 17.91$ eV

MO	$I^{(0)}$	$I^{(2)}$	$I^{(\gamma)}$	$I^{(\exp)a}$
$1\pi_g$	22.09	18.53	15.55	15.83
$3\sigma_g$	22.72	23.37	23.65	21.0
$1\pi_u$	25.76	21.33	16.72	18.8
$2\sigma_u$	41.98	38.17	37.18	—

[a] Ref. [2] (estimate from spectra of Ref. [17]).

Table 2. VIP's for HF (in eV), $\gamma = 21.82$ eV

MO	$I^{(0)}$	$I^{(2)}$	$I^{(\gamma)}$	$I^{(\exp)a}$
1π	21.27	19.64	17.58	16.05
3σ	23.13	22.80	22.26	19.9
2σ	45.54	44.22	42.71	—

[a] Ref. [1] (estimate from spectra of Ref. [12]).

Table 3. VIP's for C_2F_4 (in eV), $\gamma = 9.80$ eV

MO	$I^{(0)}$	$I^{(2)}$	$I^{(\gamma)}$	$I^{(\mathrm{exp})}$[a]
$2b_{2u}$	14.52	12.93	12.47	10.52
$6a_g$	18.76	16.33	15.51	15.95
$4b_{2g}$	20.30	17.71	16.72	16.4
$4b_{1u}$	20.91	17.39	16.13	16.6
$1a_u$	22.12	18.15	16.78	16.9
$1b_{3g}$	22.18	18.14	16.72	17.60
$5b_{3u}$	22.24	18.41	16.99	18.21

[a] Ref. [21].

Table 4. VIP's for CH_2F_2 (in eV), $\gamma = 12.35$ eV

MO	$I^{(0)}$	$I^{(2)}$	$I^{(\gamma)}$	$I^{(\mathrm{exp})}$[a]
$2b_2$	17.08	15.25	14.48	13.27
$6a_1$	18.95	16.79	15.80	—
$4b_1$	19.85	17.23	16.04	15.3
$1a_2$	21.40	17.80	16.16	15.71
$3b_1$	23.95	21.45	20.05	—
$5a_1$	25.25	22.48	20.89	18.9
$1b_2$	26.86	24.12	22.29	—

[a] Ref. [14].

Table 5. VIP's for BF_3 (in eV), $\gamma = 11.90$ eV

MO	$I^{(0)}$	$I^{(2)}$	$I^{(\gamma)}$	$I^{(\mathrm{exp})}$[a]
$1e''$	19.93	17.17	16.05	16.68
$3e'$	20.68	17.75	16.55	17.13
$1a_2'$	21.17	17.49	15.98	15.95
$2e'$	25.28	21.67	19.89	20.14
$2a_1'$	25.58	22.49	20.94	21.4
$2a_2''$	26.23	23.07	21.34	19.06

[a] Ref. [2] (interpretation of spectra from Ref. [13]).

Table 6. VIP's for CH_3F (in eV), $\gamma = 12.82$ eV

MO	$I^{(0)}$	$I^{(2)}$	$I^{(\gamma)}$	$I^{(\mathrm{exp})}$[a]
$2e$	17.56	15.67	14.76	13.05
$5a_1$	21.27	20.02	19.22	17.0
$1e$	24.12	21.61	19.98	

[a] Ref. [14].

Table 7. VIP's for CF_4 (in eV), $\gamma = 11.33$ eV

MO	$I^{(0)}$	$I^{(2)}$	$I^{(\gamma)}$	$I^{(\mathrm{exp})\,a}$
$4t_2$	20.19	17.87	16.99	17.40
$1t_1$	22.24	18.69	17.32	16.20
$1e$	23.30	19.66	18.21	18.50
$3t_2$	28.18	24.97	23.38	22.12
$4a_1$	29.47	26.85	25.58	25.12

[a] Ref. [14].

(CH_2F_2) C–H = 1.093 Å, ∢HCH = 109° 28′, C–F = 1.36 Å, ∢FCF = 108.5°; (BF_3) B–F = 1.295 Å; (CH_3F) C–H = 1.106 Å, ∢HCH = 110.0°, C–F = 1.38527 Å; (CF_4) C–F = 1.323 Å. $I^{(2)}$ are the VIP's by second order M (with approximation C), which were obtained by omitting the γ's in (13). $I^{(\gamma)}$ are the VIP's yielded by the full procedure (13). $I^{(\mathrm{exp})}$ are the experimental values for the VIP's taken from photoelectron spectra available in the literature [12–14, 17, 20–23].

The fluorine molecule (Table 1) is an example for which Koopmans' theorem breaks down: The Hartree–Fock (CNDO) level sequence $1\pi_g < 3\sigma_g < 1\pi_u$ is in contrast with the empirical $1\pi_g < 1\pi_u < 3\sigma_g$ [2, 17]. The second order VIP's $I^{(2)}$ are already correct in sequence but still far from the expected values. Better agreement with experiment is achieved by our approximation $I^{(\gamma)}$. It is remarkable to note that Koopmans' defects for F_2, calculated by our method, are of different sign in contrast to what Biskupič *et al.* [7] observed for their method. This fact obviously facilitates correcting the wrong level sequence.

In the cases of hydrogen fluoride, methylene fluoride and methyl fluoride (Tables 2, 4, 6) Koopmans' theorem yields the correct level assignment – only the numerical values are too high. This latter point is met by perturbation theory: the values $I^{(0)}$, $I^{(2)}$ and $I^{(\gamma)}$ monotonically tend towards the experimental ones.

With tetrafluoroethylene (Table 3) there is the difficulty that several of the bands lie so close together that any assignment beyond the first few levels will be somewhat arbitrary, as mentioned by Brundle *et al.* [21]. Our assignment for $2b_{2u}$ and $6a_g$ agrees with that of Brundle *et al.* [21]. For $4b_{2g}$, $4b_{1u}$, $1a_u$, $1b_{3g}$ our CNDO values according to Koopmans' theorem give the same level ordering $4b_{2g} < 4b_{1u} < 1a_u < 1b_{3g}$ as found in Ref. [21], while the VIP's obtained by perturbation theory ($I^{(2)}$, $I^{(\gamma)}$) suggest the different assignment $4b_{1u} < 4b_{2g} < 1b_{3g} < 1a_u$. The assignment in Ref. [21] was done by *ab initio* Gaussian type calculations assuming the Koopmans' defects to be 8% of the orbital energies. However, this attempt is not able to reproduce a level crossing. Our results, therefore, indicate that in this case the 8% rule for Koopmans' defects may be insufficient.

As to boron trifluoride (Table 5), there exist different assignments of the first three VIP's in the literature [13, 22, 23, 2]. Our calculations agree with the assignment of Refs. [23, 2], namely $1a_2' < 1e'' < 3e'$. One should note that this is achieved only by our final results $I^{(\gamma)}$, while $I^{(0)}$ and even $I^{(2)}$ still differ in sequence. The ordering of the higher VIP's $2e'$, $2a_1'$, and $2a_2''$ remains incorrect, but at least they come closer to the experimental values by perturbational treatment.

For carbon tetrafluoride (Table 7) the empirical level sequence is $1t_1 < 4t_2 < 1e < 3t_2 < 4a_1$ [14]. Our results agree with this, except that $1t_1$ and $4t_2$ have changed places (thus reproducing the earlier assignment of Basset *et al.* [20]), but under the perturbational treatment this error is at least reduced (cf. also Ref. [18]). For the higher VIP's, $1e$, $3t_2$, and $4a_1$ our results $I^{(0)}$, $I^{(2)}$, and $I^{(\gamma)}$ monotonically converge towards the experimental values.

In conclusion we should say that our procedure constitutes a considerable improvement over the second order approach; in its simplicity it seems promising for tackling just larger molecules, for which *ab initio* calculations are not available.

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