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Calculation of Vertical Excitation Energies of Closed-Shell Molecules in the CNDO and INDO Approximations

Christoph-Maria Liegener

Institut für Theoretische Physik der Technischen Universität, Berlin, Hardenbergstr. 4–5/IV., D-1000 Berlin 12

The Green's function method for the calculation of vertical excitation energies is adapted to the CNDO and INDO approximations by introducing an effective interaction into the irreducible vertex part. The computational scheme is explicitly developed for closed-shell molecules and applied to H_2O, H_2CO, HCOOH, $HCONH_2$.

Key words: Excitation energies – Green's functions.

1. Introduction

Early calculations of excitation energies based on the original CNDO/2 and INDO procedures [1–3] showed the necessity to include reorganization and correlation effects [4–7]. This was done by separate minimization of both ground and excited state energy [5] or by configuration interaction among the different excited states [6, 7]. In these cases the excitation energies were calculated as differences of total energies. An interesting alternative could be to calculate the excitation energies directly from orbital energies and matrix elements. Such a direct calculation of vertical excitation energies (VEE's) is provided by the particle–hole Green's function method [8–11]. If this way is chosen, it is at the same time clear, why the original CNDO/2 and INDO parametrization is preferred to spectroscopic versions as CNDO/S [12] and INDO/S [13], namely because they were adjusted to reproduce ab initio Hartree–Fock calculations which are the unperturbed problem in the Green's function method, while the latter were directly fitted to experimental data.

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Therefore, it is the purpose of the present paper to adapt the Green's function method for VEE calculation to the CNDO and INDO approximations, similarly as earlier the Green's function method for the calculation of vertical ionization potentials (VIP's) and vertical electron affinities (VEA's) has been adapted to the CNDO approximation [14–16]. For simplicity this study is limited to closed-shell molecules. However, a generalization to open-shell molecules along the lines of Ref. [17] seems also possible.

2. Theory

2.1. *Vertical Ionization Potentials and Electron Affinities*

In order to calculate the VEE's it will be necessary to know the VIP's and VEA's in the CNDO and INDO frameworks. The VIP's (and VEA's) in the CNDO framework can be calculated by the method of Ref. [16], i.e. using the following approximation for the irreducible self-energy part M:

$$M_{ij}(\omega)=\sum_{\substack{m\in occ\\ k,l\notin occ}}\frac{V_{imkl}(V_{kljm}-V_{klmj})}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l+\gamma}+\sum_{\substack{m\notin occ\\ k,l\in occ}}\frac{V_{imkl}(V_{kljm}-V_{klmj})}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l-\gamma} \tag{1}$$

where ε_m are the CNDO orbital energies, V_{imkl} the CNDO molecular two-particle integrals, γ is the arithmetic mean of all occuring CNDO Coulomb two-particle atomic integrals γ_{AB}, occ denotes the index set of occupied spin orbitals.

Eq. (1) is closely related to Cederbaum's approximation [18–20]:

$$M_{ij}(\omega)=\sum_{\substack{m\in occ\\ k,l\notin occ}}\frac{V_{imkl}(V_{kljm}-V_{klmj})}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l-\Delta_{mkl}}+\sum_{\substack{m\notin occ\\ k,l\in occ}}\frac{V_{imkl}(V_{kljm}-V_{klmj})}{\omega+\varepsilon_m-\varepsilon_k-\varepsilon_l+\Delta_{mkl}} \tag{2}$$

with

$$\Delta_{mkl}=V_{kl[kl]}-V_{km[km]}-V_{lm[lm]}$$

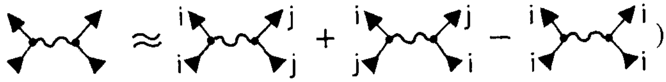
$$V_{kl[kl]}=V_{klkl}-V_{kllk}.$$

One can obtain Eq. (1) by setting $V_{ijkl}\to\gamma\delta_{ik}\delta_{jl}$ in the denominator of Eq. (2). Vice versa, Eq. (2) may be regarded as a natural generalization of Eq. (1) when going from the CNDO to a more accurate framework, in our case the INDO. (Since Eq. (2) was originally derived for the ab initio framework [18–20], the special method for VEE calculation of the next section should also be applicable with ab initio values if Eq. (2) is used for VIP calculation.)

It will be convenient for later comparison with the method for VEE calculation to complete the approximation scheme for VIP/VEA calculation of Ref. [16] by corresponding prescriptions for the INDO case:

A. Renormalization is disregarded in the irreducible self-energy part M.
B. The two-particle integrals V_{ijkl} in the irreducible interaction part I are approximated in the CNDO framework by $V_{ijkl}\approx\gamma\delta_{ik}\delta_{jl}$ (diagrammatically

) and in the INDO framework by $V_{ijkl} \approx V_{ijij}\delta_{ik}\delta_{jl} + V_{ijji}\tilde{\delta}_{il}\tilde{\delta}_{jk}(1-\delta_{ij})$ where the $\tilde{\delta}_{jk}$ are Kronecker symbols referring to the spatial parts of the adherent indices only (diagrammatically



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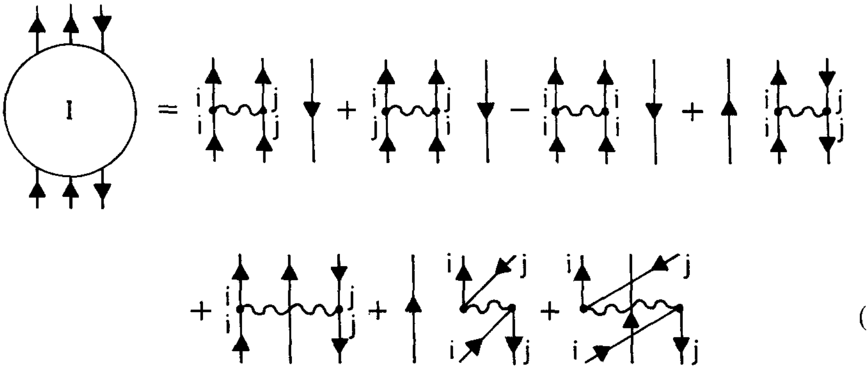
C. The irreducible self-energy part M is assumed to be nearly diagnonal.

Indeed, the irreducible interaction part I for the INDO case is then found to be



(3)

and proceeding as in Ref. [16] the expression (2) for M follows. Eqs. (1) and (2) can, of course, be simplified by performing the spin summations (since only closed-shell molecules are considered), the resulting formulae being well-known from Refs. [16] and [18], respectively.

Finally, the negative VIP's ω_k ($k \in occ$) and negative VEA's ω_k ($k \notin$occ) are calculated from the inverse Dyson equation. Since the pole strengths P_k [21] are with approximation C determined by

$$P_k^{-1} = 1 - \frac{\partial M_{kk}}{\partial \omega}(\omega_k), \tag{4}$$

the improved iteration algorithm of Ref. [22] is efficiently applied to the numerical solution of the Dyson equation.

2.2. *Vertical Excitation Energies*

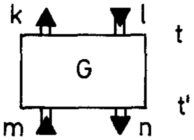
The VEE's of a molecule are defined as $E_n - E_0$, where E_n is the total electronic energy of the excited state, E_0 that of the ground state, both related to the same geometry. These energy differences can be obtained as poles of the Fourier transformed particle-hole Green's function $G_{klmn}(\omega)$ (cf. e.g. Ref. [10], p. 559). For convenience the definition of G_{klmn} is repeated here [10]:

$$iG_{klmn}(t) = \langle\Psi_0|T\{a_l^+(t)a_k(t)a_m^+(0)a_n(0)\}|\Psi_0\rangle \tag{5}$$

where Ψ_0 is the exact many-electron ground state function, a_l^+ and a_k are the

Heisenberg creation and annihilation operators of MO states l and k respectively; T is Wick's time ordering operator.

The diagram technique [10] manages a simple description of G_{klmn}; diagrams are to be labelled and read in the following way (in units with $\hbar = 1$):

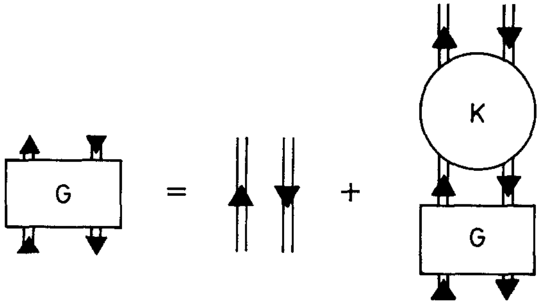


gives a factor $iG_{klmn}(t-t')$

gives a factor $iG_{kl}(t-t')$

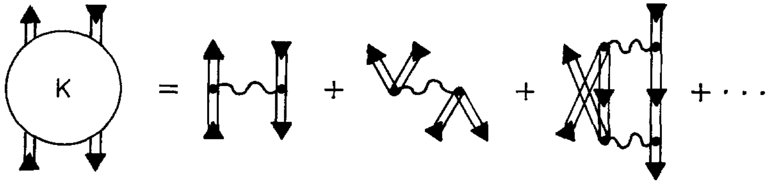
gives a factor $-iV_{klmn}$.

All inner indices have to be summed over, and all inner times have to be integrated over; closing the diagram for G_{klmn} (by connecting the indices k with l and m with n) the closed loops can be counted and the diagram obtains a factor (-1) for each loop.
Application of perturbation theory to G_{klmn} yields the graphical Bethe–Salpeter equation [9] (omitting the vertically disjoint $\omega = 0$ component [10]):



(6)

The diagram part K is called the irreducible vertex part; it is irreducible in such a sense, that its diagrams cannot be split by cutting two double lines at the same level [9]. The expansion of K starts with:



(7)

It is now in time to adapt to the CNDO and INDO frameworks by introducing the following approximations:

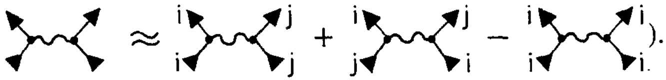
A′. For the one-particle Green's function G_{kl} the damping-free quasi-particle form with one-pole approximation is assumed [9, 21], i.e. the double lines are to be read as:

$$i\tilde{G}_{kl}(t)=\begin{cases}\delta_{kl}P_k\,e^{-i\omega_k t} & \text{for } k\notin\text{occ},\ t>0\\ -\delta_{kl}P_k\,e^{-i\omega_k t} & \text{for } k\in\text{occ},\ t\leq 0\end{cases}$$

where ω_k are the negative VIP's/VEA's and P_k the pole strengths, calculated according to the prescriptions of the preceding section.

B′. The two-particle integrals V_{ijkl} in the irreducible vertex part K are approximated in the CNDO framework by $V_{ijkl}\approx\gamma\delta_{ik}\delta_{jl}$ (diagrammatically

) and in the INDO framework by $V_{ijkl}\approx V_{ijij}\delta_{ik}\delta_{jl}+V_{ijji}\tilde{\delta}_{il}\tilde{\delta}_{jk}(1-\delta_{ij})$ (diagrammatically



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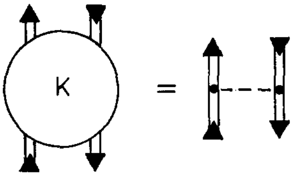
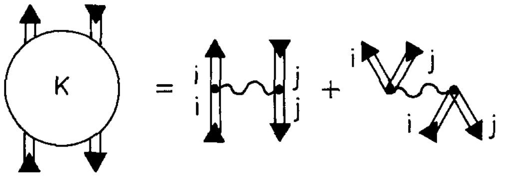
Approximation A′ establishes the connection to the VIP/VEA calculation. Approximation B′ is the analog to approximation B of the preceding section and has a similar effect, namely, that the expansion of K terminates; it is then in the CNDO framework



(8)

while in the INDO framework



(9)

It will be sufficient in the following to explicitly write down only the INDO expressions and then to find the CNDO result by analogy. Thus, inserting Eq. (9) into Eq. (6), one easily reads off:

$$\begin{aligned} iG_{klmn}(t) &= -i\tilde{G}_{km}(t)\,i\tilde{G}_{nl}(-t)\\ &\quad+\sum_{pqrs}\int_{-\infty}^{\infty} dt'\, i\tilde{G}_{kp}(t-t')\,i\tilde{G}_{ql}(t'-t)\\ &\quad\cdot\left(-iV_{psrq}\delta_{pr}\delta_{qs}+iV_{psqr}\tilde{\delta}_{pr}\tilde{\delta}_{qs}\right)iG_{rsmn}(t'). \end{aligned} \tag{10}$$

For the Fourier transformed functions one has:

$$G_{klmn}(\omega)=\frac{\bar{n}_k n_l - n_k \bar{n}_l}{\omega-(\omega_k-\omega_l)} P_k P_l \delta_{km}\delta_{nl}$$
$$+\sum_{pqrs}\frac{\bar{n}_k n_l - n_k \bar{n}_l}{\omega-(\omega_k-\omega_l)} P_k P_l \delta_{kp}\delta_{ql}$$
$$\cdot(-V_{psrq}\delta_{pr}\delta_{qs}+V_{psqr}\tilde{\delta}_{pr}\tilde{\delta}_{qs})G_{rsmn}(\omega) \qquad (11)$$

where $n_k=1$ for $k\in\text{occ}$, $n_k=0$ for $k\notin\text{occ}$ and $\bar{n}_k=1-n_k$. The poles of $G_{klmn}(\omega)$ are the zeros of the eigenvalues of its inverse, determined by [10]:

$$\sum_{mn}\left[\frac{\omega-(\omega_k-\omega_l)}{\bar{n}_k n_l - n_k \bar{n}_l}\cdot\frac{\delta_{km}\delta_{nl}}{P_k P_l}+V_{knml}\delta_{km}\delta_{ln}-V_{knlm}\tilde{\delta}_{km}\tilde{\delta}_{ln}\right]X_{mn}=0. \qquad (12)$$

The case $k\notin\text{occ}$, $l\in\text{occ}$ is considered first:

$$\left(\frac{\omega_k-\omega_l-\omega}{P_k P_l}-V_{klkl}\right)X_{kl}+\sum_{mn}V_{knlm}\tilde{\delta}_{km}\tilde{\delta}_{ln}X_{mn}=0. \qquad (13)$$

Obviously the sum in Eq. (13) runs only over spins, while for the spatial parts $k=m$, $l=n$ holds. So the secular determinant of this equation factors and we have for each pair of spatial orbitals k, $l(k\notin\text{occ}, l\in\text{occ})$ a 4×4 minor, spanned by the four pairs of spin orbitals $(k\uparrow, l\uparrow)$, $(k\downarrow, l\downarrow)$, $(k\uparrow, l\downarrow)$, $(k\downarrow, l\uparrow)$, namely:

$$\begin{vmatrix} \frac{\omega_k-\omega_l-\omega}{P_k P_l}-V_{kl[kl]}, & V_{kllk}, & 0, & 0 \\ V_{kllk}, & \frac{\omega_k-\omega_l-\omega}{P_k P_l}-V_{kl[kl]}, & 0, & 0 \\ 0, & 0, & \frac{\omega_k-\omega_l-\omega}{P_k P_l}-V_{klkl}, & 0 \\ 0, & 0, & 0, & \frac{\omega_k-\omega_l-\omega}{P_k P_l}-V_{klkl} \end{vmatrix} \qquad (14)$$

Therefore, among the roots of the characteristic equation of Eq. (13), the following four (termed ω_{kl}) arise from the above minor:

$$\omega_{kl}=\omega_k-\omega_l-P_k P_l(V_{kl[kl]}\mp V_{kllk}) \qquad (15)$$

where the upper sign describes a single, the lower sign a triply degenerate eigenvalue.

The second case ($k\in\text{occ}$, $l\notin\text{occ}$) can be handled by renaming indices $k\leftrightarrow l$ [10] and then analogously gives rise to poles $-\omega_{kl}$ which correspond to the deexcitation processes.

Eq. (15) can be reduced to the formula for singlet and triplet excitation energies in the MO picture [23]

$$\varepsilon_{kl} = \varepsilon_k - \varepsilon_l - (V_{kl[kl]} \mp V_{kllk}) \tag{16}$$

if one inserts the zeroth order quantities $\omega_k \to \varepsilon_k$, $P_k \to 1$; this shows the present Eq. (15) to be a natural generalization of Eq. (16).

Applying the same argumentations to the CNDO case one arrives at one quartly degenerate eigenvalue:

$$\omega_{kl} = \omega_k - \omega_l - P_k P_l \gamma. \tag{17}$$

The missing singlet-triplet splitting in Eq. (17) might be surprising at first sight, but seems reasonable from the following facts: In the CNDO framework there often occurs ($n\pi^*$ transitions) an accidental degeneracy of singlet and triplet energies [4–7, 12] due to additional constants of motion [24]; in case the singlet–triplet splitting is nonzero it is often ($\pi\pi^*$ transitions) too large but shows a tendency to decrease compared with *ab initio* calculations [6]. These phenomena are obviously induced by the strange behaviour of exchange matrix elements in the CNDO approximation [3, 6]. Since, on the other hand, the experimental splittings are small and of about the same order of magnitude as the inaccuracies of the CNDO procedure, it is tempting to neglect them at all.

3. Applications

It remains now to study the numerical results. Therefore, the theory is applied to four closed-shell molecules: water, formaldehyde, formic acid and formamide. The CNDO/2 and INDO orbital energies and LCAO coefficients of these molecules are calculated by the library program of Dobosh [25] assuming the following experimental geometries [26]: (H_2O, symm. C_{2v}) H—O = 0.9572 Å, $\measuredangle$HOH = 104.52°; (H_2CO, symm. C_{2v}) C—H = 1.12 Å, C—O = 1.21 Å, $\measuredangle$HCH = 118°; (HCOOH, symm. C_s) C—H = 1.085 Å, C—O′ = 1.245 Å, C—O = 1.312 Å, O—H = 0.95 Å, $\measuredangle$HCO′ = 117.8°, $\measuredangle$OCO′ = 124.3°, $\measuredangle$COH = 107.8°; ($HCONH_2$, symm. C_s) C—H = 1.094 Å, C—O = 1.243 Å, C—N = 1.343 Å, N—H = 0.995 Å, $\measuredangle$HNH = 118.98°, $\measuredangle$NCO = 123.58°, $\measuredangle$NCH = 103.9°.

In a next step, the negative VIP's and VEA's ω_k are calculated using the irreducible self-energy parts of Eq. (1) and (2). Finally, the excitation spectrum is evaluated from Eq. (16) for the unperturbed quantities ε_{kl} and from Eq. (17) and (15) for the VEE's after perturbation theory ω_{kl} in the CNDO and INDO framework respectively. The results are then compared with experimental data. It should be recalled here that CNDO and INDO are rather approximate procedures and one should not expect a very close fit of the final results with experiment.

To begin with, the calculated VIP's of the water molecule (Table 1) approach the experimental ones, if perturbation theory is applied. For the VEE's (Table 2)

Table 1. VIP's and VEA's for H_2O (in eV) $\gamma = 17.70$ eV

MO	Type	CNDO ε_k	ω_k	INDO ε_k	ω_k	exp [27, 15] $-I_k$
$2b_2$	σ^*	9.53	8.76	9.66	9.08	—
$4a_1$	σ^*	9.12	8.17	8.30	7.82	—
$1b_1$	n	−17.83	−13.88	−16.30	−13.72	−12.78
$3a_1$	σ	−19.40	−16.78	−17.55	−16.05	−14.83
$1b_2$	σ	−21.42	−20.39	−21.27	−20.61	−18.72

Table 2. VEE's for H_2O (in eV)

Excitation	Type	CNDO ε_{kl}	ω_{kl}	INDO ε_{kl}	ω_{kl}	exp [28–30] E_{kl}
$^1B_1$ $(4a \leftarrow 1b_1)$	$n\sigma^*$	9.49	8.81	9.10	8.54	7.4
$^1A_2$ $(2b_2 \leftarrow 1b_1)$	$n\sigma^*$	9.97	9.29	9.55	9.34	9.1
$^1A_1$ $(4a_1 \leftarrow 3a_1)$	$\sigma\sigma^*$	11.62	11.05	12.12	11.94	9.7
$^1B_2$ $(2b_2 \leftarrow 3a_1)$	$\sigma\sigma^*$	12.10	11.52	12.38	12.52	—
$^1B_2$ $(4a_1 \leftarrow 1b_2)$	$\sigma\sigma^*$	14.41	13.88	17.38	17.68	—
$^1A_1$ $(2b_2 \leftarrow 1b_2)$	$\sigma\sigma^*$	14.86	14.34	20.06	20.31	—
$^3B_1$ $(4a_1 \leftarrow 1b_1)$	$n\sigma^*$	9.49	8.81	7.54	7.24	7.2
$^3A_2$ $(2b_2 \leftarrow 1b_1)$	$n\sigma^*$	9.97	9.29	8.80	8.73	—
$^3A_1$ $(4a_1 \leftarrow 3a_1)$	$\sigma\sigma^*$	11.62	11.05	9.80	9.93	—
$^3B_2$ $(2b_2 \leftarrow 3a_1)$	$\sigma\sigma^*$	12.10	11.52	10.44	10.87	—
$^3B_2$ $(4a_1 \leftarrow 1b_2)$	$\sigma\sigma^*$	14.41	13.88	13.67	14.41	—
$^3A_1$ $(2b_2 \leftarrow 1b_2)$	$\sigma\sigma^*$	14.86	14.34	14.56	15.56	—

there is also a clear improvement by perturbation theory in both the CNDO and INDO framework. The experimental values of Refs. [28–30] have been assigned by comparison with the nonempirical (NE) calculations of Buenker and Peyerimhoff [31] (Table 9). Only those experimental values are listed which then correspond to the transitions calculated in Table 2. It is furthermore interesting to compare the present results (denoted as CNDO/GF and INDO/GF) for this and the other molecules with the results of CNDO/CIS [6] or INDO/SECI [32] calculations (i.e. CNDO or INDO with singly excited configuration interaction, Table 9). This shows that the behavior of the results of these methods is somewhat similar to that of the present ones, particularly in yielding the $\pi\pi^*$ transitions often too high. The singlet-triplet splitting in the INDO case seems to be decreased by the present approach. This is a general feature going from the ε_{kl} to ω_{kl} because $P_k < 1$ in Eq. (15).

As to formaldehyde, there is good agreement for the first and third VIP's ($2b_2$ and $5a_1$) with experiment (Table 3). The second VIP ($1b_1$) is only slightly moved by perturbation theory, therefore falling behind $5a_1$, but yet coming closer to the experimental value. For the excitation spectrum (Table 4) the experimental values of Refs. [34, 35] for the singlets and of Ref. [36] for the triplets have been assigned

Table 3. VIP's and VEA's for H_2CO (in eV) $\gamma = 13.31$ eV

MO	Type	CNDO		INDO		exp [33, 20]
		ε_k	ω_k	ε_k	ω_k	$-I_k$
$7a_1$	σ^*	12.94	11.87	12.26	11.76	—
$3b_2$	σ^*	8.67	7.39	8.88	8.27	—
$6a_1$	σ^*	6.22	4.77	5.88	5.24	—
$2b_1$	π^*	4.21	3.95	4.40	4.41	—
$2b_2$	n	−14.52	−11.12	−13.69	−10.90	−10.9
$1b_1$	π	−18.54	−17.47	−18.43	−17.71	−14.5
$5a_1$	σ	−20.31	−16.73	−18.71	−16.04	−16.2

Table 4. VEE's for H_2O (in eV)

Excitation	Type	CNDO		INDO		exp [34–36]
		ε_{kl}	ω_{kl}	ε_{kl}	ω_{kl}	E_{kl}
$^1A_2\ (2b_1 \leftarrow 2b_2)$	$n\pi^*$	5.01	5.33	4.95	4.99	4.1
$^1B_1\ (2b_1 \leftarrow 5a_1)$	$\sigma\pi^*$	9.60	11.44	9.26	9.81	9.0
$^1B_2\ (6a_1 \leftarrow 2b_2)$	$n\sigma^*$	12.19	6.07	11.06	9.28	7.10
$^1B_1\ (6a_1 \leftarrow 1b_1)$	$\pi\sigma^*$	13.67	12.53	13.97	14.66	—
$^1B_2\ (7a_1 \leftarrow 2b_2)$	$n\sigma^*$	13.87	14.03	13.53	13.20	—
$^1A_1\ (3b_2 \leftarrow 2b_2)$	$n\sigma^*$	14.67	8.85	14.22	12.46	7.97
$^1A_1\ (2b_1 \leftarrow 1b_1)$	$\pi\pi^*$	15.45	11.79	15.93	16.74	—
$^1A_2\ (3b_2 \leftarrow 1b_1)$	$\pi\sigma^*$	15.60	15.31	16.01	16.95	—
$^1B_1\ (7a_1 \leftarrow 1b_1)$	$\pi\sigma^*$	16.43	20.47	17.19	19.24	—
$^1A_1\ (6a_1 \leftarrow 5a_1)$	$\sigma\sigma^*$	16.79	12.18	15.47	14.09	—
$^1B_2\ (3b_2 \leftarrow 5a_1)$	$\sigma\sigma^*$	18.31	14.95	17.20	16.14	—
$^1A_1\ (7a_1 \leftarrow 5a_1)$	$\sigma\sigma^*$	21.41	20.09	19.93	19.57	—
$^3A_2\ (2b_1 \leftarrow 2b_2)$	$n\pi^*$	5.01	5.33	4.48	4.62	3.75
$^3A_1\ (2b_1 \leftarrow 1b_1)$	$\pi\pi^*$	7.62	11.79	7.27	9.97	6.20
$^3B_1\ (2b_1 \leftarrow 5a_1)$	$\sigma\pi^*$	9.60	11.44	8.26	9.05	—
$^3B_2\ (6a_1 \leftarrow 2b_2)$	$n\sigma^*$	9.93	6.07	8.77	7.44	7.00
$^3A_1\ (3b_2 \leftarrow 2b_2)$	$n\sigma^*$	12.10	8.85	11.46	10.25	—
$^3B_1\ (6a_1 \leftarrow 1b_1)$	$\pi\sigma^*$	13.67	12.53	13.10	13.96	—
$^3B_2\ (7a_1 \leftarrow 2b_2)$	$n\sigma^*$	13.77	14.03	12.48	12.40	—
$^3A_2\ (3b_2 \leftarrow 1b_1)$	$\pi\sigma^*$	15.60	15.31	15.70	16.70	—
$^3A_1\ (6a_1 \leftarrow 5a_1)$	$\sigma\sigma^*$	15.86	12.18	14.04	12.96	—
$^3B_1\ (7a_1 \leftarrow 1b_1)$	$\pi\sigma^*$	16.43	20.47	16.03	18.36	—
$^3B_2\ (3b_2 \leftarrow 5a_1)$	$\sigma\sigma^*$	17.84	14.95	16.61	15.69	—
$^3A_1\ (7a_1 \leftarrow 5a_1)$	$\sigma\sigma^*$	18.40	20.09	16.72	17.18	—

[37, 38] by comparison with the NE calculations of Ref. [38] (Table 9). It is remarkable that the ω_{kl} in the CNDO framework give the correct level sequence for the singlets $^1A_2 < {}^1B_2 < {}^1A_1 < {}^1B_1$, although it was entirely different for the ε_{kl}. In the INDO framework the ordering $^1A_2 < {}^1B_1 < {}^1B_2 < \cdots < {}^1A_1$ of the ε_{kl} is improved to $^1A_2 < {}^1B_2 < {}^1B_1 < {}^1A_1 < \cdots$ for the ω_{kl} in which only $^1B_1$ and $^1A_1$ would have to change places. The triplets are reasonably reproduced with the

exception of $^3A_1$ which is too large as a consequence of the worse approximated second VIP.

The photoelectron spectrum [33] of formic acid is shown in Table 5. The calculated VIP's ($-\omega_k$) are better in the CNDO than in the INDO framework, but also in the latter case still satisfactory. For the VEE's (Table 6) the experimental values of Ref. [39] are taken with the assignments of Ref. [39, 40]. The ω_{kl} in the

Table 5. VIP's and VEA's for HCOOH (in eV) $\gamma = 11.99$ eV

MO	Type	CNDO ε_k	ω_k	INDO ε_k	ω_k	exp [33] $-I_k$
$13a'$	σ^*	10.72	9.31	10.49	9.83	—
$12a'$	σ^*	8.42	6.09	8.07	6.32	—
$11a'$	σ^*	6.37	4.67	5.74	4.66	—
$3a''$	π^*	4.43	4.77	4.83	5.27	—
$10a'$	n	−14.71	−10.06	−13.71	−9.79	−11.51
$2a''$	π	−15.11	−12.84	−14.43	−12.30	−12.5
$9a'$	σ	−17.43	−14.13	−16.09	−13.47	−14.7

Table 6. VEE's for HCOOH (in eV)

Excitation	Type	CNDO ε_{kl}	ω_{kl}	INDO ε_{kl}	ω_{kl}	exp [39] E_{kl}
$^1A''$ $(3a'' \leftarrow 10a')$	$n\pi^*$	5.82	6.39	5.85	5.54	5.7
$^1A''$ $(3a'' \leftarrow 9a')$	$\sigma\pi^*$	9.85	9.94	9.30	9.55	—
$^1A''$ $(11a' \leftarrow 2a'')$	$\pi\sigma^*$	11.39	8.76	10.30	9.34	—
$^1A''$ $(12a' \leftarrow 2a'')$	$\pi\sigma^*$	12.70	10.63	11.91	10.81	—
$^1A'$ $(11a' \leftarrow 10a')$	$n\sigma^*$	12.83	6.51	11.34	8.46	7.6
$^1A'$ $(3a'' \leftarrow 2a'')$	$\pi\pi^*$	13.06	8.63	13.08	12.72	8.4
$^1A''$ $(13a' \leftarrow 2a'')$	$\pi\sigma^*$	14.11	13.62	13.94	13.60	—
$^1A'$ $(11a' \leftarrow 9a')$	$\sigma\sigma^*$	14.33	10.07	12.77	11.08	—
$^1A'$ $(12a' \leftarrow 10a')$	$n\sigma^*$	14.90	8.35	13.50	10.26	—
$^1A'$ $(12a' \leftarrow 9a')$	$\sigma\sigma^*$	15.74	11.93	14.60	12.67	—
$^1A'$ $(13a' \leftarrow 10a')$	$n\sigma^*$	16.23	11.35	15.23	12.95	—
$^1A'$ $(13a' \leftarrow 9a')$	$\sigma\sigma^*$	17.45	14.92	16.57	15.46	—
$^3A''$ $(3a'' \leftarrow 10a')$	$n\pi^*$	5.82	6.39	5.40	5.20	—
$^3A'$ $(3a'' \leftarrow 2a'')$	$\pi\pi^*$	6.76	8.63	6.46	7.54	—
$^3A''$ $(3a'' \leftarrow 9a')$	$\sigma\pi^*$	9.85	9.94	8.83	9.18	—
$^3A'$ $(11a' \leftarrow 10a')$	$n\sigma^*$	11.22	6.51	9.85	7.36	—
$^3A''$ $(11a' \leftarrow 2a'')$	$\pi\sigma^*$	11.39	8.76	9.79	8.95	—
$^3A''$ $(12a' \leftarrow 2a'')$	$\pi\sigma^*$	12.70	10.63	11.46	10.48	—
$^3A'$ $(11a' \leftarrow 9a')$	$\sigma\sigma^*$	13.37	10.07	11.38	10.00	—
$^3A''$ $(13a' \leftarrow 2a'')$	$\pi\sigma^*$	14.11	13.62	13.51	13.27	—
$^3A''$ $(12a' \leftarrow 9a')$	$\sigma\sigma^*$	14.51	11.93	13.23	11.66	—
$^3A'$ $(12a' \leftarrow 10a')$	$n\sigma^*$	14.56	8.35	12.87	9.82	—
$^3A'$ $(13a' \leftarrow 10a')$	$n\sigma^*$	14.61	11.35	13.17	11.43	—
$^3A'$ $(13a' \leftarrow 9a')$	$\sigma\sigma^*$	16.47	14.92	15.26	14.43	—

CNDO framework agree with these. In the INDO framework the VEE for $^1A''n\pi^*$ is good, but the $^1A'\pi\pi^*$ transition comes out too high. This behaviour seems to be a general feature of the INDO calculations.

For formamide Koopmans' theorem breaks down in the CNDO framework: The empirical level sequence of the VIP's I_k is $10a' < 2a'' < 9a'$ [29], while that of the negative CNDO orbital energies ($-\varepsilon_k$) is $2a'' < 10a' < 9a'$. The correct sequence in that case is obtained by perturbation theory (Table 7). In the INDO framework

Table 7. VIP's and VEA's for $HCONH_2$ (in eV) $\gamma = 11.19$ eV

MO	Type	CNDO ε_k	ω_k	INDO ε_k	ω_k	exp [33] $-I_k$
$13a'$	σ^*	9.03	6.44	8.83	6.73	—
$12a'$	σ^*	7.32	5.31	7.29	5.89	—
$11a'$	σ^*	6.41	4.15	5.81	4.33	—
$3a''$	π^*	5.08	5.06	5.56	5.63	—
$2a''$	π	−13.56	−11.16	−12.76	−10.61	−10.51
$10a'$	n	−13.64	−9.25	−12.65	−8.90	−10.13
$9a'$	σ	−17.57	−14.33	−16.42	−13.54	−14.2

Table 8. VEE's for $HCONH_2$ (in eV)

Excitation	Type	CNDO ε_{kl}	ω_{kl}	INDO ε_{kl}	ω_{kl}	exp [36, 42] E_{kl}
$^1A''\ (3a'' \leftarrow 10a')$	$n\pi^*$	6.01	6.47	6.03	5.56	5.65
$^1A''\ (11a' \leftarrow 2a'')$	$\pi\sigma^*$	9.69	7.34	9.01	7.77	7.8
$^1A''\ (3a'' \leftarrow 9a')$	$\sigma\pi^*$	10.73	10.81	10.10	10.32	—
$^1A''\ (12a' \leftarrow 2a'')$	$\pi\sigma^*$	11.15	8.42	10.55	9.27	—
$^1A''\ (13a' \leftarrow 2a'')$	$\pi\sigma^*$	11.63	9.81	10.90	9.55	—
$^1A'\ (3a'' \leftarrow 2a'')$	$\pi\pi^*$	12.23	7.90	12.20	11.52	7.32
$^1A'\ (11a' \leftarrow 10a')$	$n\sigma^*$	12.35	5.90	11.06	7.93	6.80
$^1A'\ (12a' \leftarrow 10a')$	$n\sigma^*$	13.43	6.98	12.43	9.34	—
$^1A'\ (13a' \leftarrow 10a')$	$n\sigma^*$	14.42	8.36	13.45	10.05	—
$^1A'\ (11a' \leftarrow 9a')$	$\sigma\sigma^*$	15.80	10.81	14.84	12.51	—
$^1A'\ (12a' \leftarrow 9a')$	$\sigma\sigma^*$	16.21	11.89	15.31	13.26	—
$^1A'\ (13a' \leftarrow 9a')$	$\sigma\sigma^*$	18.21	13.28	17.61	14.89	—
$^3A''\ (3a'' \leftarrow 10a')$	$n\pi^*$	6.01	6.47	5.64	5.27	5.30
$^3A'\ (3a'' \leftarrow 2a'')$	$\pi\pi^*$	6.61	7.90	6.20	6.89	(6.60)
$^3A''\ (11a' \leftarrow 2a'')$	$\pi\sigma^*$	9.69	7.34	8.03	7.03	—
$^3A''\ (3a'' \leftarrow 9a')$	$\sigma\pi^*$	10.73	11.38	9.46	9.85	—
$^3A''\ (12a' \leftarrow 2a'')$	$\pi\sigma^*$	11.15	8.42	10.26	9.05	—
$^3A'\ (11a' \leftarrow 10a')$	$n\sigma^*$	11.50	5.90	11.12	7.25	—
$^3A''\ (13a' \leftarrow 2a'')$	$\pi\sigma^*$	11.63	9.81	10.49	9.25	—
$^3A'\ (12a' \leftarrow 10a')$	$n\sigma^*$	11.83	6.98	10.63	8.03	—
$^3A'\ (13a' \leftarrow 10a')$	$n\sigma^*$	14.19	8.36	13.01	9.74	—
$^3A'\ (11a' \leftarrow 9a')$	$\sigma\sigma^*$	14.53	10.81	13.50	11.55	—
$^3A'\ (12a' \leftarrow 9a')$	$\sigma\sigma^*$	15.26	11.89	14.29	12.51	—
$^3A'\ (13a' \leftarrow 9a')$	$\sigma\sigma^*$	17.02	13.28	16.41	14.06	—

Table 9. Comparison with other calculations (VEE's in eV)

Excitation		CNDO/GF[a]	INDO/GF[a]	CNDO/CIS[b]	INDO/SECI[c]	NE[d]	Exp[e]
H_2O:	$^1B_1$	8.81	8.54	—	8.15	7.30	7.4
	$^1A_2$	9.29	9.34	—	8.72	9.20	9.1
	$^1A_1$	11.05	11.94	—	10.83	9.80	9.7
	$^3B_1$	8.81	7.24	—	6.72	6.90	7.2
H_2CO:	$^1A_2$	5.33	4.99	5.02	4.65	3.81	4.1
	$^1B_2$	6.07	9.28	11.27	10.41	7.38	7.10
	$^1A_1$	8.85	12.46	11.44	11.81	8.11	7.97
	$^1B_1$	11.44	9.81	9.61	9.14	9.03	9.0
	$^3A_2$	5.33	4.62	—	4.06	3.41	3.75
	$^3A_1$	11.79	9.97	—	7.21	5.56	6.20
	$^3B_2$	6.07	7.44	—	8.31	7.32	7.00
HCOOH:	$^1A''$	6.39	5.54	5.58	6.02	5.80	5.7
	$^1A'$	6.51	8.46	—	10.02	—	7.6
	$^1A'$	8.63	12.72	—	—	9.52	8.4
$HCONH_2$:	$^1A''$	6.47	5.56	5.91	—	4.08	5.65
	$^1A'$	5.90	7.93	10.78	—	6.39	6.80
	$^1A'$	7.90	11.52	11.02	—	10.49	7.32
	$^1A''$	7.34	7.77	7.72	—	7.26	7.8
	$^3A''$	6.47	5.27	5.91	—	3.80	5.30
	$^3A'$	7.90	6.89	6.99	—	4.41	(6.60)

[a] This work (ω_{kl} values of Tables 2, 4, 6, 8).
[b] Ref. [6].
[c] Ref. [32].
[d] Following Refs.: H_2O[31], H_2CO [36], HCOOH [41], $HCONH_2$ [42].
[e] Refs. as in Tables 2, 4, 6, 8.

both the ε_k and ω_k are correctly arranged. Table 8 gives the calculated VEE's and the corresponding experimental values from Refs. [36, 42]. The triplet at 6.60 eV has been enclosed in brackets because this value belongs to an unresolved peak [36] which also, and sometimes exclusively [43], has been assigned as $n\sigma^*(n3s)$ triplet. In any case, the present triplet sequence $n\pi^* < \pi\pi^*$ is at least consistent with more accurate NE calculations (Table 9). The singlets in the CNDO framework are satisfactory in magnitude, although $n\pi^*$ should change places with $n\sigma^*$ and also $\pi\pi^*$ with $\pi\sigma^*$. However, this drawback is not too serious because the corresponding energies lie fairly close together, and so their differences come into the range of inaccuracies implicit in the CNDO approximations. The situation is similar in the INDO framework: the $n\sigma^*$ and $\pi\sigma^*$ singlets should change places, but can be considered as quasi-degenerate. The other two VEE's behave like in formic acid, i.e. the $n\pi^*$ singlet is good, but $\pi\pi^*$ comes out to high. It should be noted that this is in parallel to the NE calculations (Table 9). The same holds for the still overestimated singlet-triplet splitting in this case.

In conclusion one can summarize that the main advantage of the present method lies in its simplicity, permitting an easy and direct calculation of both low-lying VIP's and VEE's in a well-defined approximation.

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