

MNDO-EHP method for the calculation of vertical excitation energies

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Abstract. Applicability of the unmodified MNDO theory to the low-lying excited singlet and triplet states is tested through an adaptation of the single excitation electron-hole potential (EHP) method to the theory. The method is both structurally and computationally very simple and has the useful feature of orbital picture for the excited states. The agreement, in the transition energies and also in the relative ordering of various excited states, obtained by our method and from the extended CI method, is very good. There is some problem in convergence arising out of symmetry breaking in cases of degeneracy in the ground state SCF wavefunction.

Keywords. MNDO; excited state; electron-hole potential; vertical transition energy; semiempirical model Hamiltonian.

1. Introduction

The scope for semiempirical calculation of molecular valence excitation energies is obvious (Hase *et al* 1978; Lauer *et al* 1978; Schweig and Thiel 1981; Schultz *et al* 1985; Ertl and Leska 1988). The remarkable success of the MNDO (Dewar and Thiel 1977) method in calculating the important ground state properties of molecules has led to attempts to make an explicit inclusion of electron correlation in a semiempirical frame, so that a reasonable estimate of the different excited state energies may be obtained. 3×3 CI calculations with the usual MNDO half-electron (HE) MOs (Dewar *et al* 1968) have produced very low excited states. This shortcoming has been attributed (Baird and Hadley 1986) to an underestimation of the 'antibondingness' of the HE antibonding MOs. The lack of variational stability of the HE wavefunction has also been pointed out (Dewar and Olliviella 1979). To circumvent these difficulties several methods like MNDO-CI and MNDO-SDCI have been proposed. The purpose of such extension has been to achieve an "exact" solution of the semiempirical model Hamiltonian (Thiel 1981a), thus invoking a very large volume of computation. This however did not result in the desired degree of accuracy as found in the LNDO/S method. Thiel (1981b) proposed a method, MNDOC, in which electron correlation is recovered through higher orders of perturbation and a reparametrization as well. But the method fails to produce fruitful results because the application of such a powerful tool within a limited domain of the valence basis AOs makes no significant difference. Keeping in mind the extra stability of HE antibonding MOs

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and the variational inexactness of the occupied wavefunction, we propose to formulate a simple but variationally optimized MNDO SCF wavefunction for the electronically excited singlet and triplet states. Apart from explicit inclusion of electron correlation into the MNDO method, no development has so far taken place to tailor it in the direction of excited state SCF calculations. The electron hole potential (EHP) method (Morokuma and Iwata 1972) has been applied with success in the study of excited state energetics in weak processes like hydrogen bonding (Iwata and Morokuma 1973). In a model study of excitation energies in thiocarbonyls, the present authors have found encouraging application (Banerjee and Chandra 1987) of the EHP method to the CNDO/2 theory.

2. Method

Details of the EHP method have been described by Morokuma and coworkers (Morokuma and Iwata 1972; Iwata and Morokuma 1973b). In this method the excited singlet and triplet wavefunctions are represented by

$${}^{1,3}\Phi(i \rightarrow k) = |\phi_1 \bar{\phi}_1 \dots \sqrt{\frac{1}{2}}(\phi_i \bar{\phi}_k \mp \bar{\phi}_i \phi_k) \dots \bar{\phi}_n \bar{\phi}_n|. \quad (1)$$

The MO set $\{\phi_i\}$ consists of the EHP MOs which are obtainable from the closed shell RHF MOs $\{\psi_3\}$ by means of the transformations

$$\phi_i = \sum_j^{\text{occ}} d_{ij} \psi_j, \quad (2)$$

$$\phi_k = \sum_l^{\text{vac}} g_{kl} \psi_l. \quad (3)$$

Variational optimization of energy of the singly excited ($i \rightarrow k$) state, as given by (1), with respect to the expansion coefficients d_{ij} and g_{kl} produces the eigenvalue equation

$$\tilde{F} \phi_m = \varepsilon_m \phi_m, \quad (4)$$

where

$$\tilde{F}(i \rightarrow k) = F + Q\Omega_{1i}Q + P\Omega_{2k}P. \quad (5)$$

F is the Hartree-Fock (HF) operator, P is the projection operator for the occupied HF space and $Q = 1 - P$.

$$P = \sum_i^{\text{occ}} |\psi_i\rangle \langle \psi_i|, \quad (6)$$

$$\Omega_{1i} = a_1 J_i + b_1 K_i; \quad \Omega_{2k} = a_2 J_k + b_2 K_k. \quad (7)$$

The numbers a_1, b_1, a_2, b_2 are fixed according to the symmetry of the excited state. For a singlet, $a_1 = -1, b_1 = 0, a_2 = 1, b_2 = 0$; and for a triplet, $a_1 = -1, b_1 = 2, a_2 = 1, b_2 = -2$.

The matrix form of (5) in the orthonormal valence AO basis (χ) is

$$\tilde{F} = F + (1 - P) V_{1i}(1 - P) + P V_{2k} P, \quad (8)$$

in which overlap is neglected in the normalisation according to the basic premises of MNDO theory. The Hermitian matrices V_{1i} and V_{2k} are obviously $V_{1i} = \chi^+ \Omega_{1i} \chi$ and $V_{2k} = \chi^+ \Omega_{2k} \chi$.

At the level of NDDO approximations, the one-centre and two-centre matrix elements of the matrix V_m can be written as,

$$(V_m)_{\mu\mu}^A = \sum_v^A (a \langle \mu\mu | vv \rangle + b \langle \mu v | \mu v \rangle) C_{vm}^2 + a \sum_{B \neq A} \sum_{\alpha\sigma}^B \langle \mu\mu | \alpha\sigma \rangle C_{am} C_{\sigma m}, \quad (9)$$

$$(V_m)_{\mu\nu}^A = [(2a + b) \langle \mu\nu | \mu\nu \rangle + b \langle \mu\mu | \nu\nu \rangle] C_{\mu m} C_{\nu m} + a \sum_{B \neq A} \sum_{\alpha\sigma}^B \langle \mu\nu | \alpha\sigma \rangle C_{am} C_{\sigma m}, \quad (10)$$

$$(V_m)_{\mu\alpha}^{AB} = b \sum_v^A \sum_{\sigma}^B \langle \mu\nu | \alpha\sigma \rangle C_{vm} C_{\sigma m}. \quad (11)$$

The coefficient matrix C_m corresponds to the HF MO ψ_m .

After constructing \tilde{F} the next task is to diagonalise it,

$$\tilde{F} \tilde{C}_m = \varepsilon_m \tilde{C}_m. \quad (12)$$

The transformed coefficient matrix \tilde{C}_m gives rise to the EHP orbitals

$$\phi_m = \chi \tilde{C}_m. \quad (13)$$

The method is clearly an iterative one and after convergence, the excited state energy is calculated as

$$E = E_o + \varepsilon_k - \varepsilon_i - a_1 J_{ik} + b_1 K_{ik}. \quad (14)$$

It has been shown (Iwata and Morokuma 1973b) that the EHP wavefunction can be expanded in terms of singly excited configurations with the product of the variational parameters d_{ij} and g_{kl} as coefficients,

$$\Phi^{\text{EHP}} = (i \rightarrow k) = \sum_j^{\text{occ}} \sum_I^{\text{vac}} d_{ij} g_{kl} \psi(\psi_j \rightarrow \psi_i). \quad (15)$$

Contrary to the SECI wavefunction,

$$\Phi^{\text{SECI}} = \sum_j^{\text{occ}} \sum_I^{\text{vac}} C_{ji} \psi(\psi_j \rightarrow \psi_i), \quad (16)$$

the EHP wavefunction in (15) is equivalent to that from the Tamm–Dancoff approximation (Dunning and Mckoy 1967) which takes into account the mixing of single excitations of the appropriate symmetry. As a result there is rearrangement of the total charge density during the excitation. There may be observed an orbital relaxation in the process. The orbital relaxation energy can be estimated through a comparison with the excitation energy obtained from MNDO virtual orbitals under the single transition approximation (Roothaan 1951). In table 1 we present the orbital relaxation energies for the various excitations of the molecules investigated. A detailed description of the excited state electron density is omitted in the present work.

Table 1. Vertical excitation energies (eV).

Molecule	State (excitation)	MNDO-EHP	EHP relaxation energy	MNDO ^a SDCI(SECI)	Expt. ^b
C ₂ H ₄	¹ B _{1u}	5.81	0.000	6.05(5.63)	7.65
	(b _{3u} → b _{2g} [*])				
	³ B _{1u}	2.21	0.001	2.54(2.12)	4.4
	¹ B _{1g}	6.48	0.000	6.70(6.28)	9.18
H ₂ CCHF	(b _{3g} → b _{2g} [*])				
	³ B _{1g}	6.21	0.000	—	—
H ₂ CCF ₂	¹ A'	5.38	0.002	5.64(5.24)	7.19
	(a'' → a'' [*])				
H ₂ CO	³ A'	1.84	0.057	2.24(1.83)	4.39
	¹ A ₁	5.13	0.002	5.43(5.02)	7.59
F ₂ CO	(b ₁ → b ₁ [*])				
	³ A ₁	1.63	0.065	2.04(1.62)	4.59
	¹ A ₂	3.04	0.070	3.13(3.04)	4.2
	(n → π [*])				
F ₂ CS	³ A ₂	2.62	0.093	2.84(2.62)	3.3
	¹ A ₁	8.76	0.000	6.86(6.83)	8.7–10.5
	(π → π [*])				
	³ A ₁	4.69	0.000	4.94(4.64)	5.6–6.2
trans- CH ₂ CHCHO	¹ A ₂	4.30	0.022	4.12(4.32)	5.2–6.9
	(n → π [*])				
	³ A ₂	3.87	0.033	3.90(3.90)	—
	¹ A ₁	7.86	0.001	—	—
cis- CH ₂ CHCHO	(π → π [*])				
	³ A ₁	4.24	0.139	—	—
	¹ A ₂	2.34	0.000	—	—
	(n → π [*])				
HCCCHO	³ A ₂	2.03	0.001	—	—
	¹ A ₁	4.86	0.000	—	—
	(π → π [*])				
	³ A ₁	1.99	0.021	—	—
trans- CH ₂ CHCHO	¹ A''	2.96	1.339	3.10(2.96)	3.21
	(n → π [*])				
	³ A''	2.54	1.520	2.78(2.07)	3.00
	¹ A'	5.39	0.036	5.40(5.20)	6.40
cis- CH ₂ CHCHO	(π → π [*])				
	³ A'	2.10	0.756	2.41(2.54)	—
	¹ A''	2.96	1.255	—	—
	(n → π [*])				
HCCCHO	³ A''	2.54	1.427	—	—
	¹ A'	5.25	0.005	—	—
	(π → π [*])				
	³ A'	2.12	0.716	—	—
HCCCHO	¹ A''	3.11	1.050	3.13(3.11)	3.56
	(n → π [*])				
	³ A''	2.67	1.178	2.73(2.67)	2.99
	¹ A'	6.23	0.048	4.46(4.38)	—
HCCCHO	(π → π [*])				
	³ A'	3.51	0.913	3.26(3.18)	—

(Continued)

Table 1. (Continued)

Molecule	State (excitation)	MNDO-EHP	EHP relaxation energy	MNDO* SDC1(SECI)	Expt. ^b
CH ₃ CHO	¹ A''	2.95	0.197	2.98(2.95)	4.28
	(n → π*)				
	³ A''	2.52	0.233	2.62(2.52)	—
	¹ A'	8.25	0.316	6.69(6.75)	9.0
H ₂ NCHO	(π → π*)				
	³ A'	4.45	1.108	—	—
	¹ A''	3.93	0.030	3.91(3.94)	5.70
	(n → π*)				
H ₂ CCO	³ A''	3.54	0.040	3.57(3.51)	5.30
	¹ A'	6.35	0.017	—	—
	(π → π*)				
	³ A'	3.74	0.290	—	—
H ₂ CNN	¹ A ₂	1.99	0.054	2.00(1.99)	3.84
	(b ₁ → b ₂ [*])				
	³ A ₂	1.74	0.060	1.89(1.73)	—
	¹ A ₁	5.29	0.022	4.85(4.58)	6.78
	(b ₁ → b ₁ [*])				
	³ A ₁	1.87	0.024	—	—
HNNH	¹ B ₁	5.38	0.174	5.82(5.29)	5.85
	(b ₁ → a ₁ [*])				
	¹ B _g	2.86	0.013	3.30(2.86)	3.55
	(a _g → b _g [*])				
H ₂ CNN	³ B _g	1.95	0.016	6.52(1.95)	—
	¹ B _u	8.65	0.000	8.30(7.79)	—
	(a _u → b _g [*])				
	³ B _u	4.03	0.000	—	—
trans- Butadiene	¹ A ₂	1.65	0.091	1.70(1.64)	3.14
	(b ₁ → b ₂ [*])				
	³ A ₂	1.24	0.150	1.50(1.23)	—
	¹ A ₁	5.27	0.009	4.77(4.36)	5.70
(CHO) ₂	(b ₁ → b ₁ [*])				
	¹ B _u	4.79	0.000	5.20(4.59)	5.92
	(b _g → a _u [*])				
	³ B _u	2.45	0.000	2.21(1.60)	3.2
(CHO) ₂	¹ A _g	5.92	0.000	6.70(5.84)	5.8
	(b _g → b _g [*])				
	³ A _g	4.05	0.000	3.12(2.42)	4.93
	¹ A _u	3.07	0.005	2.39(2.38)	2.73
(CHO) ₂	(a _g → a _u [*])				
	³ A _u	2.73	0.016	1.97(1.96)	2.38
	¹ B _g	4.74	0.014	3.21(3.19)	3.72
	(a _g → b _g [*])				
	³ B _g	4.51	0.020	2.75(2.73)	—

(Continued)

Table 1. (Continued)

Molecule	State (excitation)	MNDO-EHP	EHP relaxation energy	MNDO SDCI(SECI)	Expt. ^b
Cyclopentadiene	1B_2 ($a_2 \rightarrow b_1^*$)	3.82	0.002	4.31(3.70)	5.20
	3B_2	2.00	0.034	2.05(1.50)	3.10
	1A_1 ($a_2 \rightarrow a_2^*$)	5.59	0.000	3.79(5.20)	—
	1A_1 ($b_1 \rightarrow b_1^*$)	6.00	0.003	6.45(6.18)	7.9
	1B_2 ($a_2 \rightarrow b_1^*$)	3.07	0.001	3.14(3.02)	3.44
Fulvene	3B_2	1.78	0.354	1.56(1.26)	—
	1A_1 ($b_1 \rightarrow b_1^*$)	4.64	0.028	4.35(4.37)	5.28
	1A_1 ($a_2 \rightarrow a_2^*$)	5.52	0.000	—	—
	1B_2 ($a_2 \rightarrow b_1^*$)	4.42	0.000	4.62(4.13)	—
	3B_2	2.24	0.001	2.26(1.76)	3.99
Furan	1A_1 ($a_2 \rightarrow a_2^*$)	5.21	0.001	3.46(4.56)	—
	1A_1 ($b_1 \rightarrow b_1^*$)	5.65	0.002	6.19(6.14)	—
	1B_2 ($a_2 \rightarrow b_1^*$)	4.76	0.001	4.19(3.89)	4.7
	1B_1 ($a_1 \rightarrow b_1^*$)	4.45	0.522	5.05(4.42)	4.31
	1A_2 ($a_1 \rightarrow a_2^*$)	4.74	0.017	5.34(4.72)	—
Pyridine	1A_1 ($a_1 \rightarrow a_2^*$)	5.48	0.110	5.58(4.0)	6.16
	1A_1 ($b_1 \rightarrow b_1^*$)	3.19	0.156	2.65(2.04)	4.1

^aErtl and Leska (1988); ^bcited in Ertl and Leska (1988).

However, the magnitude of the relaxation energy depends upon the particular excited state which is specified in this model by the symmetries of the pair of orbitals involved in the excitation. Due to orbital relaxation in the excited state, the EHP wavefunction is more suitable for the calculation of one-electron properties.

3. Computational procedure

The calculation is accomplished in two parts. First, a ground state geometry optimization of the closed-shell molecule is performed by the standard MNDO method. This is followed by an iterative EHP calculation using the ground state vectors, repulsion integrals, core integrals and first-order density matrices which are saved at the end of the ground state calculations. A level shifting technique (Saunders and Hillier 1973) is used at each step of iteration. This ensures the intra-subspace

transformations in (2) and (3) and any subspace crossing is thereby prevented. The problem of swapping of orbitals of the selected symmetry types during EHP iterations is controlled by a technique (Banerjee and Chandra 1987) of symmetry array handling. This ensures convergence corresponding to the desired excitation.

4. Results and discussion

In table 1 we present our results for the vertical transition energies (VTE) of 20 simple molecules, many of which have been previously studied in a similar context (Ertl and Leska 1988). It has already been noted earlier (Schweig and Thiel 1981; Baird and Hadley 1986; Ertl and Leska 1988) that electronic excited states are systematically underestimated by the MNDO and MNDOC methods, the effect being more pronounced in the former. We report that our EHP calculated results are capable of providing a good comparison with available experimental VTE. In most of the cases our MNDO-EHP excitation energies are close to those from SDCI or SECI results (Ertl and Leska 1988). Wide differences in the position of the ${}^1A_1(a_2a_2^*)$ state has been reported in the SDCI and SECI calculated values for cyclopentadiene and furan. Most notably, the 3B_g state in HNNH has been predicted to be much higher (VTE 6.52 eV) than the corresponding singlet! In that respect our EHP calculated magnitudes appear to represent the proper sequence. In $(\text{CHO})_2$ the MNDO-EHP VTE are uniformly higher than the SDCI, MNDOC and experimental values. As a possible source of this discrepancy we have pointed out that the MNDO eigenvalue of the LUMO a_u^* orbital in $(\text{CHO})_2$ is -0.58 eV which is quite unrealistic for a neutral molecule.

In ethylene and substituted ethylenes the singlet $n\pi^*$ and $\pi\pi^*$ states are reproduced relatively better than the triplets. This deficiency of triplets is much reduced in the carbonyl compounds. In ring compounds, including heterocycles like furan and pyridine, the results from our calculation are more consistent with the experimental ones, as compared to the SDCI results. Moreover, the $n\pi^*$ states (1B_1 and 1A_2) in pyridine, which are predicted (Ertl and Leska 1988) above the $\pi\pi^*$ states by the SDCI method, are found to lie below the $\pi\pi^*$ states (1B_2 and 1A_1) according to our calculations. Due to the advantage of designating a particular orbital pair for a given transition, a convenient chemical sense can be attributed to the excited states and also to the corresponding one-electron densities. During EHP iterations, convergence to a state of proper symmetry is maintained by appropriately locating the concerned orbital pair which sometimes change their respective ordering, particularly when the higher energy transitions are sought for. EHP convergence could not be attained in the case of single excitation from an orbital belonging to a degenerate pair to an upper orbital of degenerate type. Such a situation arose for HOMO to LUMO transition in acetylene and allene. This failure to convergence can be attributed to loss of symmetry of the EHP wavefunction upon excitation.

Finally, the efficacy of the present method can be understood through a comparison of the computational times required by this method and by the direct CI one. Our method involves matrix operations (product and diagonalisation) with matrices having size no greater than $N \times N$, where N is the basis size. In the direct CI method the dimension of the CI matrix increases so rapidly with N that it becomes very difficult to carry out CI(SDCI) calculations for even the medium-sized molecules like furan

Table 2. A comparison of computational time.

Basis size N	Molecule	Time for MNDO-EHP calculation (s)	Time for truncated DCI calculation (s)
10	H ₂ CO	57(³ A ₂ state)	92
12	C ₂ H ₄	63(³ B _{1u} state)	160
16	F ₂ CO	158(³ A ₂ state)	615
20	<i>trans</i> - CH ₂ CHCHO	454(³ A" state)	2145
24	Furan	413(³ B ₂ state)	5242

All calculations were performed on an HP-1000 micro-computer.

or pyridine. Moreover, the computation of matrix elements for V_1 and V_2 matrices (8) is much simpler than those of CI. In table 2 we present the computation times required by the MNDO-EHP and by the truncated double excitation CI (DCI) which is only a part of the full SDCI calculation.

5. Conclusion

Characteristic of the electron-hole potential (EHP), the present method generates modified MOs appropriate to the particular single excitation chosen. Such orbitals enjoy greater preference in describing an excited state than the picture provided with the help of Hartree-Fock orbitals which were used in constructing the SDCI configurations. In considering the excited state molecular geometries, preference should naturally be paid to the EHP wavefunction, as compared to the Hartree-Fock HE wavefunction. This feature of studying the excited state potential energy surface is under investigation.

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