

Semi-Empirical All Valence Electrons SCF-MO-CNDO Theory

III. Orbital Energies and Ionization Potentials*

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Orbital energy levels, calculated by the semi-empirical SCF-MO-CNDO theory developed previously, are compared with experimental ionization potentials assuming that Koopmans' theorem is valid. Most of the energy levels are in much better agreement with experiment than those calculated from either the Pople-Segal CNDO/2 theory or the Extended Hückel Theory. The results are used to assign observed ionization potentials to specific molecular orbitals for molecules for which this assignment has not been determined experimentally.

Mit unserer SCF-MO-CNDO-Methode berechnete Orbitalenergien werden mit experimentellen Ionisationspotentialen verglichen. Die Übereinstimmung ist besser als bei der erweiterten Hückel- oder der CNDO/2-Methode von Pople und Segal.

Les niveaux d'énergie orbitale calculés à l'aide de la théorie semiempirique SCF-MO-CNDO, sont comparés avec les potentiels expérimentaux d'ionisation en admettant la validité de le théorème de Koopmans. La plupart des niveaux d'énergie sont en meilleur accord avec l'expérience que lesquels calculés selon la méthode Pople-Segal CNDO/2 ou la méthode d'Hückel étendue. Puis on a coordonné les résultats avec des orbitales moléculaires.

A. Introduction

The SCF-MO-CNDO theory is useful for all-valence-electron calculations when the molecule is too large to be treated by the Roothaan equations [1, 10] since the three and four centered integrals are removed. Either the parameters derived theoretically [2–5] or the empirical parameters described in the first two papers of the series [6, 7] can be used in the SCF-MO-CNDO theory. In paper II [7] it was shown that the empirical parameters were better for predicting bonding energies in molecules. Now we consider their success in determining orbital energies, that is to say ionization potentials.

The identity between orbital energies and ionization potential depends on the validity of Koopmans' theorem, according to which the energy required to remove an electron from the i^{th} orbital of a molecule, leaving the nuclei fixed and the orbitals unaltered, is given by

$$I_i = -E_i \quad (1)$$

if both the molecular and ionic wave functions satisfy the Hartree-Fock, or the Roothaan, equations and if differences in correlation energy can be neglected [1].

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E_i is the energy eigenvalue of the i^{th} orbital, found by solving the secular equations. Peters [8] has shown that the E_i correspond more closely to experimental ionization potentials than do energies of localized orbitals.

Cotton's notation [11] has been used for symmetry groups and their irreducible representations. For the C_{2v} and D_{2h} groups, the assignment of axes is arbitrary, and standard notation [12] has been used for planar molecules. The only non-planar molecules of these two symmetry groups considered are C_3H_8 and B_2H_6 , for which the choice of axes is stated later.

B. Experimental Ionization Potentials

Calculated orbital energies are compared with ionization potentials determined by photoelectron spectroscopy when they are available, and by threshold methods for other molecules.

Orbital energy levels should be compared with vertical ionization potentials. If no vibrational structure is resolved, as in electron impact [15, 18], the observed ionization threshold does not necessarily correspond to either the vertical or the adiabatic ionization process [15]. If vibrational structure is resolved, as in photoelectron spectroscopy [9, 13, 14], the peak corresponding to the lowest ionization energy gives the adiabatic ionization potential, and the most intense peak corresponds to the vertical ionization potential. Only in the recent work of Turner and May [20] were the intensities obtained accurately enough so that vertical ionization potentials could be determined.

The bonding molecular orbitals of the molecules considered (CO_2 , OCS , CS_2 , NNO) have vertical and adiabatic ionization potentials which differ by a few tenths of an electron volt [20]. In all other molecules, the ionization potentials determined by photoelectron spectroscopy are adiabatic.

For molecules with many distinct orbital energies in the range observed by photoelectron spectroscopy, molecular orbital theory often predicts groups of orbitals closely spaced in energy, which correspond to a single observed ionization potential. In such cases it is assumed [21, 22], that the observed ionization potential corresponds to several ionic states which have not been resolved.

C. Comparison of Calculated Orbital Energies with Ionization Potentials

The energies of occupied molecular orbitals, are listed in Tables 1, 2 and 3 for a number of molecules, and compared with experimental ionization potentials. Results calculated using different sets of parameters are listed in different columns, which are identified by the symbols listed in Table 4.

The molecular symmetry groups, and the irreducible representation of each calculated orbital, are listed in the first column on the left. Experimental information concerning the symmetry of the orbitals is given next to the experimental potentials. When no such information is available, the experimental ionization potentials are listed in numerical order, and do not necessarily correspond to the calculated orbitals in the same rows. Experimental ionization potentials in parentheses refer to uncertain values.

Table 1. Comparison of the SCF-MO orbital energies in eV of first row molecules with the experimental ionization potentials. a) as calculated using the CNDO approximation and empirical bonding parameters (columns M2, O2, and R2); b) as calculated by different theories (columns MP, OP, and RP). Where there are no results in the table this is due to lack of convergence to self-consistency

Parameter set		M2	O2	R2	MP	OP	RP	Exptl. I.P.	Ref.
Molecule	Orbit. sym. (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	
H ₂ (D _{∞h})	σ _g	-14.69	-15.44	-18.62	-17.11	-18.60	-20.09	15.45	[23]
LiH(C _{∞v})	σ	-8.09	-7.90	-9.94	-12.34	-13.21	-13.15	(7.81-7.91)	[24]
BeH ₂ (D _{∞h})	σ _u	-11.41	-11.77	-13.43	-16.27	-17.26	-17.89		
	σ _g	-12.74	-12.83	-14.79	-17.15	-18.07	-18.85		
BH ₃ (D _{3h})	e'	-12.11	-12.85	-14.89	-16.80	-17.94	-19.16	11.4	[25]
	a ₁ '	-17.73	-17.78	-20.54	-24.56	-25.63	-26.91		
CH ₄ (T _d)	t ₂	-12.70	-13.50	-15.64	-17.05	-18.34	-19.78	12.99	[26, 18]
	a ₁	-23.51	-23.40	-26.16	-32.32	-33.56	-34.68	(24.00)	
NH ₃ (C _{3v})	a ₁	-12.45	-13.30	-15.47	-13.26	-14.00	-16.30	10.35	[14]
	e	-13.56	-14.20	-16.58	-17.75	-19.22	-20.21	14.95	
	a ₁	-27.07	-26.71	-30.50	-34.59	-35.89	-37.08		
H ₂ O(C _{2v})	b ₁	-14.11	-14.33	-17.90	-14.11	-14.72	-17.83	b ₁ 12.61	[26]
	a ₁	-14.03	-14.88	-17.25	-16.10	-17.11	-19.38	14.23	
	b ₂	-14.68	-15.36	-17.85	-18.64	-20.22	-21.44	18.02	
	a ₁	-32.69	-32.51	-35.84	-37.87	-39.03	-40.46		
HF(C _{∞v})	π	-16.19	-16.67	-20.85	-16.70	-17.33	-21.28	π 16.06	[27]
	σ	-16.38	-17.30	-20.14	-19.48	-20.75	-23.14	σ 16.48	
	σ	-37.60	-37.88	-42.91	-40.87	-41.84	-45.55		
N ₂ (D _{∞h})	σ _g	-13.57	-14.25	-16.49	-15.34	-15.66	-18.30	σ _g 15.58	[28]
	π _u	-13.62	-14.44	-16.34	-18.16	-19.40	-20.38	π _u 16.70	
	σ _u	-23.15	-23.46	-25.94	-22.03	-22.03	-25.16	σ _u 18.80	
	σ _g	-30.23	-29.65	-34.00	-40.95	-41.87	-43.27		
CO(C _{∞v})	σ	-13.20	-13.81	-15.94	-14.56	-14.78	-17.26	σ 14.00	[23]
	π	-13.76	-14.40	-16.88	-18.25	-19.52	-21.09	π 16.54	
	σ	-20.83	-20.53	-22.97	-21.62	-22.00	-24.67	σ 19.65	
	σ	-33.40	-33.15	-36.50	-43.03	-44.09	-45.33		
CO ₂ (D _{∞h})	π _g	-13.78	-14.55	-17.34	-12.87	-13.88	-15.70	π _g 13.79	[20, 29]
	π _u	-16.26	-16.83	-20.51	-21.18	-22.29	-24.81	π _u 17.59	
	σ _u	-13.58	-14.55	-16.38	-17.24	-18.23	-20.43	σ _u 18.07	
	σ _g	-20.69	-21.01	-23.26	-21.03	-21.81	-24.42	σ _g 19.36	
	σ _u	-33.73	-33.81	-37.43	-41.31	-42.34	-43.99		
	σ _g	-34.67	-34.46	-38.18	-43.09	-44.06	-45.40		
NNO(C _{∞v})	π		-13.58	-15.81	-11.83	-13.14	-14.44	π 12.90	[20, 29]
	σ		-15.35	-17.88	-17.28	-18.21	-20.72	σ 16.40	
	π		-16.63	-20.18	-21.82	-22.96	-25.44	π 18.14	
	σ		-23.83	-26.22	-21.62	-22.67	-24.98	σ 20.08	
	σ		-29.54	-33.93	-38.01	-39.16	-41.03		
	σ		-34.33	-38.82	-45.14	-46.22	-48.00		
O ₃ (C _{2v})	a ₂	-14.35	-14.59		-12.05	-13.13	-14.68	12.3	[30]
	a ₁	-14.72	-15.20		-13.32	-13.83	-17.35	12.52	
	b ₂	-14.75	-15.20		-13.73	-14.29	-17.71	13.52	
	b ₁	-16.18	-16.85		-20.31	-21.40	-23.54	16.4-17.4	
	b ₂	-18.11	-18.19		-21.17	-22.14	-24.49		
	a ₁	-18.67	-18.34		-21.73	-22.36	-25.73	19.24	
	a ₁	-30.10	-30.70		-28.14	-28.40	-32.10		
	b ₂	-33.24	-33.32		-36.72	-37.57	-39.90		
	a ₁	-38.78	-37.88		-47.55	-48.35	-50.49		

Table 1 (Continued)

Parameter set	<i>M2</i>	<i>O2</i>	<i>R2</i>	<i>MP</i>	<i>OP</i>	<i>RP</i>	Exptl. I.P.	Ref.		
Molecule	Orbital sym.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	
$C_2H_2(D_{\infty h})$	π_u	-10.49	-11.38	-13.09	-15.14	-16.40	-17.46	π_u 11.40	[31]	
	σ_g	-12.33	-12.94	-14.88	-18.12	-19.35	-20.62	σ_g 16.44		
	σ_u	-18.20	-18.63	-20.59	-24.03	-25.27	-26.55	σ_u 18.42		
	σ_g	-24.20	-24.19	-26.57	-34.98	-36.17	-36.84			
$C_2H_4(D_{2h})$	b_{3u}	-10.30	-11.11	-12.72	-13.86	-15.01	-16.60	$b_{3u}(\pi)$ 10.48	[19]	
	b_{3g}	-11.10	-11.95	-13.61	-13.40	-14.54	-15.82	12.50		
	a_g	-11.63	-12.36	-14.21	-16.66	-17.84	-19.15	14.39		
	b_{2u}	-14.73	-15.25	-17.77	-22.33	-23.68	-25.11	15.63		
	b_{1u}	-19.14	-19.48	-21.61	-24.97	-26.19	-27.49	(19.13)		
	a_g	-25.43	-25.12	-27.90	-37.16	-38.30	-39.06			
$C_2H_6(D_{3d})$	e_g	-11.32	-12.26	-14.06	-13.74	-14.93	-16.32	11.49	[19, 26]	
	a_{1g}	-11.32	-12.07	-13.76	-15.94	-17.02	-18.21			
	e_u	-14.18	-14.81	-17.26	-20.63	-21.93	-23.41			14.74
	a_{2u}	-20.22	-20.52	-22.80	-26.57	-27.79	-29.07			(20.13)
	a_{1g}	-26.04	-25.60	-28.60	-38.13	-39.27	-40.08			
$C_3H_8(C_{2v})$	b_1	-10.93	-11.93	-13.63	-12.72	-13.88	-15.28	11.07	[19, 26]	
	b_2	-10.64	-11.47	-13.00	-13.78	-14.89	-16.12			
	a_1	-10.96	-11.83	-13.44	-13.42	-14.55	-15.86			
	a_2	-12.29	-13.17	-15.25	-16.16	-17.42	-18.91	13.17		
	b_2	-12.72	-13.52	-15.67	-18.10	-19.28	-20.67			
	a_1	-14.17	-14.81	-17.19	-20.76	-22.00	-23.40			
	b_1	-15.06	-15.60	-18.24	-22.67	-23.98	-25.51	15.17		
	a_1	-19.38	-19.76	-21.98	-25.94	-27.18	-28.55			
	b_2	-22.76	-22.76	-25.36	-31.80	-32.98	-34.05			
	a_1	-27.62	-26.99	-30.21	-41.86	-42.97	-43.68			
$B_2H_6(D_{2h})$	b_{3g}	- 8.82	-10.02	-11.22	- 9.14	-10.25	-10.94	12.0	[25]	
	b_{2u}	-10.65	-11.54	-13.39	-14.56	-15.96	-16.70			
	b_{3u}	-12.72	-13.63	-15.50	-19.39	-20.72	-21.20			
	a_g	-14.07	-14.47	-16.75	-21.66	-23.04	-23.64			
	b_{1u}	-17.20	-17.36	-19.96	-25.45	-26.87	-27.55			
	a_g	-21.28	-21.16	-24.38	-35.01	-36.40	-36.84			
$LiF(C_{\infty v})$	π	-10.10	-10.88	-11.02	-14.11	-15.05	-14.99			
	σ	-10.14	-10.88	-11.20	-14.17	-15.01	-15.37			
	σ	-31.22	-31.75	-33.20	-37.40	-38.38	-38.61			
$F_2(D_{\infty h})$	π_g	-17.80	-17.94	-22.97	-16.77	-16.77	-22.09	π_g 15.63	[27]	
	σ_g	-17.02	-17.66	-19.68	-20.22	-21.19	-22.72	σ_g 17.35		
	π_u	-19.42	-19.27	-24.89	-20.45	-20.45	-25.77	π_u 18.46		
	σ_u	-37.56	-37.82	-43.20	-36.12	-36.12	-41.99			
	σ_g	-41.26	-40.91	-47.43	-44.31	-44.52	-49.73			
$CH_3F(C_{3v})$	e	-12.65	-13.68	-16.02	-13.96	-14.77	-17.57	e 12.85	[32]	
	a_1	-14.11	-15.06	-16.84	-18.61	-19.70	-21.27	a_1 14.10		
	e	-15.87	-16.34	-20.38	-20.42	-21.39	-24.12	(a_1) 16.89		
	a_1	-23.15	-23.33	-26.16	-28.82	-29.83	-32.05			
	a_1	-36.87	-37.16	-42.04	-43.47	-44.40	-47.10			
$HCN(C_{\infty v})$	π	-12.44	-13.33	-15.31	-16.40	-17.71	-18.58	13.91	[33]	
	σ	-12.81	-13.72	-15.31	-15.32	-15.94	-18.15			
	σ	-20.33	-20.69	-22.74	-23.81	-24.90	-26.43			
	σ	-27.86	-27.60	-31.31	-37.55	-38.64	-39.62			

Table 1 (Continued)

Parameter set	<i>M2</i>	<i>O2</i>	<i>R2</i>	<i>MP</i>	<i>OP</i>	<i>RP</i>	Exptl. I.P.	Ref.	
Molecule	Orbital sym.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
CH ₃ CN(C _{3v})	<i>e</i>		-12.49		-13.81	-15.09	-15.89	12.22	[34]
	<i>a₁</i>		-12.32		-14.61	-15.29	-17.28		
	<i>e</i>		-14.90		-20.54	-21.97	-23.21		
	<i>a₁</i>		-18.68		-20.43	-21.53	-22.88		
	<i>a₁</i>		-24.75		-34.24	-35.45	-36.46		
	<i>a₁</i>		-27.62		-39.07	-40.19	-40.83		
FCN(C _{∞v})	<i>π</i>	-13.01	-13.97	-16.18	-14.25	-15.20	-17.14		
	<i>σ</i>	-14.85	-15.90	-17.45	-15.92	-16.51	-19.15		
	<i>π</i>	-16.94	-17.54	-21.40	-21.55	-22.49	-25.51		
	<i>σ</i>	-20.63	-21.04	-23.50	-22.87	-23.87	-26.26		
	<i>σ</i>	-28.67	-28.41	-32.53	-37.37	-38.31	-39.92		
	<i>σ</i>	-38.59	-38.86	-43.60	-46.08	-47.14	-49.85		

The main feature of Table 1 is that the orbital energies calculated using electron repulsion integrals evaluated from atomic spectra, columns *M2*, and *O2*, are in all cases higher, and in most cases in better agreement with experiment, than those calculated using theoretical electron-repulsion integrals, column *R2*. The use of theoretical electron-repulsion integrals leads to the prediction of ionization potentials which are too large in molecules, as it does in atoms. If the electron-repulsion integrals are adjusted to give the correct atomic ionization potentials and electron affinities, they also give more accurate molecular ionization potentials.

The difference between the two empirical formulae for the inter-atomic electron-repulsion integrals, γ_{AB} , is less significant since the choice affects the orbital energies by less than 1 eV in most cases. The Ohno formula leads to closer agreement with experiment in a slightly greater number of cases than the Mataga formula, but this is not conclusive evidence in favour of the Ohno formula. The results are relatively insensitive to the exact values of the γ_{AB} 's, so that the use of these approximate electron-repulsion integrals does not lead to serious error.

The value of the Slater exponent for hydrogen has even less effect upon the computed orbital energies, so that no clear choice of Z'_H could be based on them. However, since the value 1.2 leads to more accurate bonding energies [7], the columns *M2* and *O2* list the orbital energies computed using the best sets of parameters and the results computed using $Z'_H = 1.0$ are not shown explicitly.

The energies in columns *M2* and *O2* are compared with orbital energies using the Pople-Segal bonding parameters *MP*, *OP* and *RP* in Table 1, and with those calculated from the Extended Hückel Theory, *H2*, in Table 2. A comparison of columns *MP* and *OP* with columns *M2* and *O2* shows that the Pople-Segal bonding parameters lead to ionization potentials which are much higher than those obtained with empirical bonding parameters, and are in almost all cases in worse agreement with experiment. For many bonding and anti-bonding molecular orbitals, the effect of using the Pople-Segal bonding parameters is greater than that of using theoretical electron-repulsion integrals, since the ionization potentials of these orbitals in columns *MP* and *OP* are higher than the corresponding ones in

Table 2. Comparison of semi-empirical and Hartree-Fock orbital energies

Orbital energy		M2	O2	H2	Hartree-Fock	Ref.	Exptl. I.P.	
CH ₄ (T _d)	t ₂	-12.70	-13.50	-15.31	-14.72	[36]	12.99	
	a ₁	-23.51	-23.40	-24.40	-25.63		(24)	
NH ₃ (C _{3v})	a ₁	-12.45	-13.30	-14.28	-10.60	[37]	10.35	
	e	-13.56	-14.20	-16.73	-16.40		14.95	
	a ₁	-27.07	-26.71	-27.69	-30.06			
H ₂ O(C _{2v})	b ₁	-14.11	-14.33	-17.27	-13.48	[37]	b ₁	12.61
	a ₁	-14.03	-14.88	-17.78	-15.13		14.23	
	b ₂	-14.68	-15.36	-19.02	-18.54		18.02	
	a ₁	-32.69	-32.51	-33.28	-36.08			
HF(C _{∞v})	π	-16.19	-16.67	-20.86	-17.70	[35]	π	16.06
	σ	-16.38	-17.30	-21.43	-20.91		σ	16.48
	σ	-37.60	-37.88	-39.74	-43.57			
HCl(C _{∞v})	π	-13.18	-13.46		-12.96	[35]	π	12.80
	σ	-14.07	-14.79		-17.02		σ	16.28
	σ	-24.87	-25.07		-30.38			
N ₂ (D _{∞h})	σ _g	-13.57	-14.25	-14.05	-17.36	[38]	σ _g	15.58
	π _u	-13.62	-14.44	-16.24	-17.10		π _u	16.70
	σ _u	-23.15	-23.46	-19.99	-20.92		σ _u	18.80
	σ _g	-30.23	-29.65	-31.59				
CO(C _{∞v})	σ	-13.20	-13.81	-14.39	-15.08	[35]	σ	14.00
	π	-13.76	-14.40	-17.80	-17.40		π	16.54
	σ	-20.83	-20.53	-20.09	-21.87		σ	19.65
	σ	-33.40	-33.15	-39.44	-41.39			
CO ₂ (D _{∞h})	π _g	-13.78	-14.55	-17.20	-14.81	[35]	π _g	13.79
	π _u	-16.26	-16.83	-18.14	-19.45		π _u	17.59
	σ _u	-13.58	-14.55	-17.51	-20.23		σ _u	18.07
	σ _g	-20.69	-21.01	-19.56	-21.77		σ _g	19.36
	σ _u	-33.73	-33.81	-32.59	-40.19			
	σ _g	-34.67	-34.46	-35.50	-41.63			
NNO(C _{∞v})	π		-13.58	-15.27	-13.37	[35]	π	12.90
	σ		-15.35	-16.16	-19.01		σ	16.40
	π		-16.63	-18.16	-20.73		π	18.14
	σ		-23.83	-19.85	-22.63		σ	20.08
	σ		-29.54	-29.17	-38.75			
	σ		-34.33	-35.17	-43.82			
C ₂ H ₂ (D _{∞h})	π _u	-10.49	-11.38	-13.39	-11.17	[35]	π _u	11.40
	σ _g	-12.33	-12.94	-15.30	-18.58		σ _g	16.44
	σ _u	-18.20	-18.63	-19.47	-20.95		σ _u	18.42
	σ _g	-24.20	-24.19	-26.64	-28.02			
C ₂ H ₄ (D _{∞h})	b _{3u}	-10.30	-11.11	-13.07	-10.38	[39]	b _{3u} (π)	10.48
	b _{3g}	-11.10	-11.95	-14.49	-14.08		12.50	
	a _g	-11.63	-12.36	-14.48	-15.86		14.39	
	b _{2u}	-14.73	-15.25	-16.24	-17.97		15.63	
	b _{1u}	-19.14	-19.48	-20.38	-21.95		(19.13)	
	a _g	-25.43	-25.12	-26.47	-28.80			
F ₂ (D _{∞h})	π _g	-18.80	-17.94	-20.09	-18.04	[40]	π _g	15.63
	σ _g	-17.02	-17.66	-22.46	-20.30		σ _g	17.35
	π _u	-19.42	-19.27	-21.57	-21.91		π _u	18.46
	σ _u	-37.56	-37.82	-36.06	-40.68			
	σ _g	-41.26	-40.91	-42.47	-47.80			

Table 3. Comparison of orbital energies (in eV) in different MO theories for molecules with not all first row-atoms

Parameter set		M2	O2	H2	Exptl. I.P.	Ref.
SiH ₄ (T _d)	t ₂	-12.08	-12.67	-14.79	12.2	[51]
	a ₁	-18.09	-18.15	-21.18		
GeH ₄ (T _d)	t ₂	-12.12	-12.75	-14.97	12.3	[51]
	a ₁	-17.78	-18.14	-22.07		
SnH ₄ (T _d)	t ₂	-11.85	-15.42	-14.54		
	a ₁	-16.22	-20.43	-20.02		
PH ₃ (C _{3v})	a ₁	-12.18	-12.75	-11.85	10.2	[52]
	e	-12.31	-13.02	-15.04		
	a ₁	-20.88	-20.76	-21.78		
AsH ₃ (C _{3v})	a ₁	-11.72	-12.17	-10.70	10.6	[53]
	e	-11.89	-12.52	-14.43		
	a ₁	-18.20	-18.10	-20.78		
SbH ₃ (C _{3v})	a ₁	-11.42	-11.86	-10.27		
	e	-11.62	-12.18	-14.29		
	a ₁	-18.28	-18.13	-19.67		
H ₂ S(C _{2v})	b ₁	-11.64	-11.79	-12.40	10.42	[19]
	b ₂	-12.66	-13.35	-15.87	12.62	
	a ₁	-12.61	-13.25	-13.75	14.82	
	a ₁	-21.61	-21.58	-23.29	20.12	
H ₂ Se(C _{2v})	b ₁	-11.81	-11.97	-11.68	9.88	[54]
	b ₂	-12.59	-13.25	-15.55		
	a ₁	-12.59	-13.19	-13.27		
	a ₁	-20.83	-20.85	-22.91		
H ₂ Te	b ₁	-11.74	-11.85	-11.04	9.14	[34]
	b ₂	-12.33	-12.92	-15.19		
	a ₁	-12.37	-12.87	-12.90		
	a ₁	-19.83	-19.85	-21.69		
HCl(C _{∞v})	π	-13.18	-13.46	-15.04	π 12.80	[27]
	σ	-14.07	-14.79	-16.59	σ 16.28	
	σ	-24.87	-25.07	-26.19		
HBr(C _{∞v})	π	-12.09	-12.28	-13.10	π 11.87	[27]
	σ	-13.22	-13.86	-15.11	σ 15.31	
	σ	-23.58	-23.69	-24.76		
HI(C _{∞v})	π	-12.08	-12.19	-12.67	π 10.75	[27]
	σ	-12.68	-13.25	-14.82	σ 14.03	
	σ	-20.32	-20.38	-22.00		
OCS(C _{∞v})	π	-11.71	-12.26	-13.14	π 11.27	[20, 29]
	π	-14.76	-15.36	-17.76	π 15.60	
	σ	-12.97	-13.81	-14.67	σ 16.04	
	σ	-18.77	-19.32	-18.40	σ 18.00	
	σ	-24.05	-23.89	-24.25		
	σ	-33.71	-33.58	-34.37		
CS ₂ (D _{∞h})	π _g	-10.93	-11.33	-12.24	π _g 10.11	[20, 29]
	π _u	-12.73	-13.28	-14.18	π _u 12.92	
	σ _u	-12.01	-12.59	-13.48	σ _u 14.49	
	σ _g	-17.70	-18.23	-15.72	σ _g 16.19	
	σ _u	-21.35	-21.52	-21.64	(17.05)	
	σ _g	-25.42	-25.08	-26.97		
	σ	-23.77	-23.52	-25.71		
CS	π	-11.31	-11.82	-13.65		
	σ	-11.49	-11.94	-12.13		
	σ	-18.46	-18.66	-16.96		
	σ	-23.77	-23.52	-25.71		

Table 3 (Continued)

Parameter set		M2	O2	H2	Exptl. I.P.	Ref.
SO ₂ (C _{2v})	a ₁	-12.30	-12.69	-13.03	12.32	[19]
	b ₂	-12.71	-13.09	-17.07		
	a ₂	-13.31	-13.33	-17.23	13.17	
	b ₁	-15.06	-15.30	-18.00		
	b ₂	-15.32	-15.42	-17.86	16.42	
	a ₁	-15.99	-15.66	-17.89		
	a ₁	-21.59	-21.58	-19.72	(20.07)	
	b ₂	-32.63	-32.34	-32.64		
	a ₁	-33.72	-33.15	-34.82		
Cl ₂ (D _{∞h})	π _g	-13.05	-13.16	-13.80	π _g 11.50	[27, 49]
	π _u	-14.81	-14.70	-16.05	π _u 14.11	
	σ _g	-13.46	-13.94	-16.42	σ _g 15.94	
	σ _u	-23.61	-23.74	-22.04	σ _u 20.61	
	σ _g	-26.98	-26.79	-28.62		
Br ₂ (D _{∞h})	π _g	-11.74	-11.83	-11.98	π _g 10.71	[27]
	π _u	-13.21	-13.12	-14.01	π _u 12.52	
	σ _g	-12.11	-12.53	-14.36	σ _g 14.44	
	σ _u	-22.25	-22.37	-20.47		
	σ _g	-25.12	-24.94	-26.96		
I ₂ (D _{∞h})	π _g	-11.79	-11.86	-11.72	π _g 9.65	[27]
	π _u	-13.01	-12.95	-13.46	π _u 11.28	
	σ _g	-11.47	-11.85	-13.94	σ _g 12.79	
	σ _u	-19.23	-19.31	-18.40		
	σ _g	-21.55	-21.45	-23.53		
ClF(C _{∞v})	π	-14.44	-14.34	-14.78	≤ 12.7	[50]
	π	-17.24	-17.11	-20.97		
	σ	-15.14	-15.64	-20.09		
	σ	-25.82	-25.65	-24.80		
	σ	-38.16	-37.98	-40.10		
BrF(C _{∞v})	π	-13.20	-12.94	-12.91	≤ 11.9	[50]
	π	-16.29	-16.14	-20.92		
	σ	-14.14	-14.59	-19.52		
	σ	-24.37	-24.07	-23.62		
	σ	-37.25	-37.04	-39.95		
IF(C _{∞v})	π	-13.65	-13.45	-12.58	≤ 10.5	[50]
	π	-15.72	-15.57	-20.88		
	σ	-13.25	-13.67	-18.88		
	σ	-21.63	-21.39	-21.99		
	σ	-36.49	-36.31	-39.63		
BrCl(C _{∞v})	π	-12.29	-12.35	-12.53	≤ 11.1	[50]
	π	-14.00	-13.92	-15.40		
	σ	-12.70	-13.15	-15.46		
	σ	-22.84	-22.94	-21.32		
	σ	-26.02	-25.84	-27.83		
ICl(C _{∞v})	π	-12.40	-12.46	-12.24	π 10.55	[49]
	π	-13.84	-13.76	-15.29	π 12.16	
	σ	-12.35	-12.77	-15.26		
	σ	-20.52	-20.54	-19.67		
	σ	-25.04	-24.97	-26.70		
IBr(C _{∞v})	π	-11.76	-11.85	-11.84	π 10.23	[49]
	π	-13.14	-13.06	-13.75	π 11.64	
	σ	-11.77	-12.17	-14.15		
	σ	-20.12	-20.18	-19.14		
	σ	-23.96	-23.88	-25.55		

Table 3 (Continued)

Parameter set		<i>M2</i>	<i>O2</i>	<i>H2</i>	Exptl. I.P.	Ref.
CH ₃ Cl(<i>C_{3v}</i>)	<i>e</i>	-11.81	-12.41	-14.11	<i>e</i> 11.42	[32]
	<i>a₁</i>	-12.21	-12.97	-15.63	<i>a₁</i> 12.07	
	<i>e</i>	-14.18	-14.79	-16.06	<i>e</i> 13.02	
	<i>a₁</i>	-21.64	-22.02	-21.56	<i>a₁</i> 18.71	
	<i>a₁</i>	-26.03	-25.98	-27.52		
CH ₃ Br(<i>C_{3v}</i>)	<i>e</i>	-11.19	-11.61	-12.68	<i>e</i> 10.69	[32]
	<i>a₁</i>	-11.46	-12.16	-14.22	<i>a₁</i> 11.62	
	<i>e</i>	-13.76	-14.43	-15.58	<i>e</i> 12.94	
	<i>a₁</i>	-21.16	-21.51	-20.90	<i>a₁</i> 19.13	
	<i>a₁</i>	-25.22	-25.09	-26.54		
CH ₃ I(<i>C_{3v}</i>)	<i>e</i>	-11.30	-11.64	-12.35	<i>e</i> 9.80	[32]
	<i>a₁</i>	-10.99	-11.64	-13.89	<i>a₁</i> 11.22	
	<i>e</i>	-13.57	-14.24	-15.51	<i>e</i> 13.14	
	<i>a₁</i>	-18.98	-19.26	-19.55	<i>a₁</i> 19.76	
	<i>a₁</i>	-24.02	-23.91	-25.13		
ClCN(<i>C_{∞v}</i>)	<i>π</i>	-12.30	-13.08	-14.47		
	<i>σ</i>	-12.87	-13.69	-14.88		
	<i>π</i>	-14.40	-14.93	-15.77		
	<i>σ</i>	-19.48	-20.00	-17.70		
	<i>σ</i>	-25.83	-26.08	-25.79		
	<i>σ</i>	-28.68	-28.38	-29.99		
BrCN(<i>C_{∞v}</i>)	<i>π</i>		-12.40	-13.19		
	<i>σ</i>		-12.81	-14.29		
	<i>π</i>		-14.16	-15.21		
	<i>σ</i>		-19.63	-16.87		
	<i>σ</i>		-24.75	-24.67		
	<i>σ</i>		-28.00	-29.71		
ICN(<i>C_{∞v}</i>)	<i>σ</i>	-11.68	-12.36	-14.14		
	<i>π</i>	-11.92	-12.42	-12.78		
	<i>π</i>	-13.35	-13.90	-15.15		
	<i>σ</i>	-18.41	-18.83	-16.64		
	<i>σ</i>	-22.00	-22.12	-22.41		
	<i>σ</i>	-28.03	-27.73	-29.42		

Table 4

Parameter	set for computation of molecular properties
1. <i>H2</i>	Extended Hückel Theory $Z_H = 1.2$
2. <i>R2</i>	Bonding parameters β_A^0 derived from the hydride energies [7] (empirical), $Z_H = 1.2$, the interatomic γ_{AB} derived from the Roothaan integral formulae (theoretically) and the Ohno [7] and Mataga [7] formulae respectively
<i>O2</i>	
<i>M2</i>	
3. <i>RP</i>	The bonding parameters β_A^0 derived from Pople and Segal [3] (theoretical), $Z_H = 1.2$, the interatomic γ_{AB} derived from the Roothaan, Ohno [7] or Mataga [7] formulae
<i>OP</i>	
<i>MP</i>	

column *R2*. The energies of lone-pair or non-bonding orbitals, such as the a_1 and b_1 orbitals of ammonia and water respectively, are relatively insensitive to changes in the bonding parameters. The reason for this difference is clear if the orbital energy is expressed in terms of the orbital coefficients.

$$E_i = \sum_{k,l} C_{ki}^* C_{li} F_{kl}. \quad (2)$$

The only terms in the summation which depend on the bonding parameters are those involving matrix elements F_{kl} between orbitals on different atoms, and these terms are only significant if the coefficients of atomic orbitals in at least 2 atoms in the molecular orbital are large, i.e., if the orbital is a bonding (or anti-bonding) orbital.

Pople and Segal [3, 4] evaluated neither the electron-repulsion integrals, nor the bonding parameters, empirically. Orbital energies calculated with all the parameters used by Pople and Segal are listed in column *RP*, and are generally in worse agreement with experiment than those calculated using either empirical bonding parameters, or empirical electron-repulsion integrals. The only empirical parameters used by Pople and Segal are the local terms of the diagonal core Hamiltonian matrix elements, U_{ss} and U_{pp} , which are evaluated from atomic spectra [4]. Table 1 shows that this degree of empiricism is not adequate for the calculation of accurate orbital energies.

The column *H2* lists orbitals energies calculated using the Extended Hückel Theory [55]. On the whole, the EHT orbital energies are less accurate than the SCF-MO-CNDO energies in columns *M2* and *O2* although they are quite accurate for a few molecules, such as N_2 and CO. The results for the hydrides, and especially hydrogen, however, shows that the EHT is unreliable.

The semi-empirical orbital energies of some small molecules are compared in Table 2 with approximate Hartree-Fock orbital energies from exact SCF-MO calculations with extended basis sets [35, 36–40]. If Koopmans' theorem is assumed to be valid, the overall accuracy of the semi-empirical orbital energies is comparable with that of the Hartree-Fock orbital energies. Of course, the latter are far closer to exact solutions of the Hartree-Fock equations, but they are not always in good agreement with measured ionization potentials, since Koopmans' theorem does not hold exactly. In cases where the semi-empirical orbital energies are in better agreement with ionization potentials, the errors due to the approximate solution of Roothaan's equations partially cancel those due to Koopman's theorem.

Table 3 lists the orbital energies for molecules which contain atoms heavier than neon. SCF-MO-CNDO calculations for these molecules have only been made with empirical bonding parameters and electron-repulsion integrals, since empirical parameters have been shown to be better for molecules containing only light atoms in Table 1. The accuracy of the computed orbital energies is about the same for both sets of molecules, for both the SCF-MO-CNDO theory and the EHT.

In summary, therefore, the best of the semi-empirical theories considered is the SCF-MO-CNDO theory, with empirical electron-repulsion integrals and bonding parameters.

Some additional features of the orbital energies and ionization potentials are discussed below for specific molecules.

Hydrogen

In Table 1 the computed ionization potential is most accurate if γ_{AB} is given by the Ohno formula (it is independent of the Slater exponent of the atomic orbitals).

Lithium Hydride

No experimental value for the ionization potential of LiH is known. A rigorous upper bound, and a probable lower bound, for the energy of LiH^+ have been calculated exactly by Browne [24], using a generalized valence-bond wave function. Such a calculation was possible for this ion because it contains only three electrons. These bounds have been combined with the experimental energy of LiH to give the ionization potential within the limits given in the table. The ionization potentials calculated using the SCF-MO theory with empirical bonding parameters and electron-repulsion integrals are in good agreement with the value from the ab initio calculation.

Methane

The approximate value 24 eV for the second ionization potential was determined by Collin and Delwiche [18], using mass spectrometry, and is considered uncertain by the authors. An earlier value of 19.42 eV, based on the electron impact spectrum [32], has been shown to correspond to an autoionization level [18]. This conclusion has been confirmed by photoelectron spectroscopy, since no second ionization potential is observed for CH_4 below 21.21 eV [26]. It is probable, therefore, that the true second ionization potential is within 1 eV of the value (23.4 to 23.5 eV) predicted by the semi-empirical SCF-MO-CNDO theory. In the absence of the extension of photoelectron spectroscopy to higher incident photon energies, this conclusion would be supported if the predicted second ionization potentials for SiH_4 , GeH_4 and SnH_4 , which are in the range observable at present by photoelectron spectroscopy, were shown to be accurate.

Ammonia and Related Molecules

The highest occupied molecular orbital is the lone pair on nitrogen, so that its computed energy is insensitive to changes in the bonding parameters. For PH_3 , AsH_3 and SbH_3 , the two highest molecular orbital energies are predicted to be so close together that the photoelectron spectra should be examined to see how many distinct ionization potentials can be resolved. The two peaks may be further apart than predicted, however, since their spacing is seriously under-estimated in ammonia.

Water and Related Molecules

The order of the computed orbital energies depends on the choice of parameters. The b_1 orbital, a lone pair on the oxygen atom, is, in fact, the highest since the first ionization potential is much sharper than the next two in the photoelectron spectrum [26]. For H_2S , H_2Se and H_2Te , on the other hand, the b_1 orbital is

predicted to be the highest for all parameters tried. This is consistent with experiment for H_2S , for which Al-Joboury and Turner [19] assigned the first ionization to a non-bonding orbital.

Carbon Dioxide and Related Molecules

All the calculations predict that the highest σ_u orbital energy of CO_2 is higher than one or both π orbital energies, in disagreement with the experimental order of ionization potentials, which is based on the emission spectrum of the CO_2^+ ion [43]. Complete SCF-MO calculations give the correct order of orbital energies with an extended basis set [35], but not with a minimum basis set [44], so that the decrease of energy associated with improved flexibility of the wave function is greater for the σ_u orbital than for the π -orbitals. The incorrect order of orbital energies in the semi-empirical theory, consequently, may also be due to the use of a minimum basis set.

For OCS and CS_2 , the predicted order of orbital energies is again in disagreement with the experimental order, which is based on the similarity of the photoelectron spectra to that of CO_2 , and the absence, as in CO_2 , of a Rydberg series converging to the second ionization potential [29]. No complete SCF-MO calculations have been made for these molecules, but it can be assumed that the source of error is the same.

For NNO, which is isoelectronic to CO_2 , the second ionization potential has been found to correspond to a σ -orbital by photoelectron spectroscopy, so that both the semi-empirical and the complete SCF-MO theory are in agreement with experiment. The actual inversion of orbital energies on going from CO_2 to NNO may be due of the fact that the removal of the centre of symmetry allows mixing g and u orbitals, which causes a greater separation of the energetically closer σ -orbital energies than the π -orbital energies. This mixing effect is absent in the symmetric CO_2 and CS_2 , and small in OCS, but is evidently important in NNO.

Sulphur Dioxide and Ozone

No experimental information is available concerning the assignment of ionization potentials to specific orbitals, so that the predicted order cannot be verified. For SO_2 , a good fit is obtained if the first two observed ionization potentials are assumed to be three incompletely resolved peaks, and the third observed peak to correspond to three unresolved energy levels. The fourth observed ionization potential at 20.07 eV is considered uncertain by Turner [19], but its existence is supported by the theoretical prediction of an orbital at -21.6 eV.

Ethylene

The b_{3u} orbital, which has its nodal plane in the plane of the nuclei, is the π -orbital of chemistry [45, 46], and has been shown experimentally to be the highest occupied orbital [19]. It is correctly predicted to be the highest with empirical bonding parameters, but not with the Pople-Segal bonding parameters.

The fifth ionization potential is considered uncertain by Turner [19], but agrees well with the energy of the b_{1u} orbital, computed using empirical parameters.

Ethane

There are four calculated orbital energies (columns $M2$ and $O2$) higher than -21.21 eV, and three observed ionization potentials [26] in this range. Good agreement of the computed energies with experiment is obtained only if it is assumed that the observed first ionization potential corresponds to the two highest orbital energies, which are not resolved. It is clear from the observed photoelectron spectrum [26] of C_2H_6 that two peaks as close as the predicted orbital energies either would not be resolved, or would be interpreted as the vibrational structure of a single peak. Dewar and Klopman [21] have made the same assumption in order to fit calculated orbital energies to the observed ionization potentials.

Propane

The irreducible representations are labelled assuming that the z -axis is the twofold symmetry axis, and the x -axis is normal to the plane of the three carbon atoms. The first three observed ionization potentials are assumed to correspond to seven calculated orbital energies. Dewar and Klopman [21] also calculated seven orbital energies above -16 eV.

Diborane

The irreducible representations are labelled assuming that the z -axis lies along the boron-boron line, and the x -axis connects the two bridge hydrogens. The atomic orbitals on the bridge hydrogens participate in the a_g and b_{3u} orbitals, which provide the bridge bonding corresponding to the "three centre bonds" in the localized-orbital description [47] of B_2H_6 .

Halogens

The σ_g -orbital is predicted to be the highest occupied orbital in F_2 and I_2 , according to the semi-empirical SCF-MO-CNDO theory, and the second highest in Cl_2 and Br_2 , whereas the photoelectron spectra [27] show that it is below one orbital in F_2 , and both in the other halogens. Complete SCF-MO calculations for F_2 , using either an extended [40] or a minimum [48] basis, predict the correct order of orbital energies, so that the error in the semi-empirical theory must be due to either the CNDO approximation or the choice of parameters. The orbital energies calculated with Pople-Segal bonding parameters are in the correct order, but are in error by several eV as for other molecules.

Interhalogens

For the interhalogen molecules, the highest σ -orbital energy in the SCF-MO-CNDO theory is also higher than one or both-orbital, energies, in disagreement with the experimental observation of spin-orbit splitting of the first two ionization potentials of ICl and IBr [49].

For ClF , BrF , IF and $BrCl$, experimental ionization potentials have not been determined, but upper bounds to the first ionization potential, determined from appearance potentials in halogen mixtures [50], are listed.

Methyl Fluoride

Frost and McDowell [32] list the third ionization potential as a_1 in their table, but their accompanying text indicates that this is a misprint, and that the third highest orbital has e symmetry, as in the other methyl halides, and in agreement with all versions of MO theory considered.

Hydrogen Cyanide and Methyl Cyanide

The computed orbital energies indicate that the first two ionization potentials may be too close to be resolved. This prediction could be verified by determining how many distinct ionization potentials are resolved in the photoelectron spectra, which have not yet been observed.

D. Conclusions

The SCF-MO-CNDO theory leads to the prediction of fairly accurate ionization potentials when empirical electron-repulsion integrals and bonding parameters are used and is definitely more reliable than the EHT. The theory is, of course a drastic semi-empirical approximation to the complete SCF-MO theory in which an extended basis set is used and all the electron-interaction integrals are evaluated explicitly; even in this theory the ionization potentials are not predicted exactly (Table 2) due to errors in Koopman's Theorem. It is therefore not surprising that some of the predicted orbital energies in the semi-empirical SCF-MO theory are in error or even in the wrong order for a given molecule.

The computed orbital energies provide support, but not conclusive evidence, for a given assignment of the ionization potentials of a molecule when this order has not been determined experimentally.

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