Theoret. chim. Acta (Berl.) 27, 63—68 (1972)

Relationes

A.M.O. Calculations for Some First Row Diatomic Molecules

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Received March 23, 1972

AMO wavefunctions for LiH, Li_2, HF, F_2 are presented.

An explicit formula for computing the energy of a closed shell system composed by doubly occupied MO's and singly filled AMO's is given.

The AMO-method provides a simple tool to construct partially correlated wavefunctions for molecules and crystals [1–2]. It is a version of the Different Orbitals for different spin method particularly suited for molecular systems and can be considered as a particular case of the general EHF scheme. Because of the relatively small amount of computations involved it is convenient for studying large size molecules and there is no doubt that its most useful applications are concerned with systems too large to be treated with more accurate procedures.

Nevertheless the AMO technique found interesting applications also in the field of small molecular systems [3–7]. In this case an essential advantage of the AMO w.f. over the one-determinant approximation is a correct asymptotic behaviour for large internuclear distances. Thanks to this property AMO is one of the simplest theoretical tools to compute potential energy curves or surfaces. Moreover *ab initio* AMO calculations on small systems are useful tests of the accuracy of the method. An exaustive discussion on this point would involve the optimization of the molecular orbitals to be paired to build the AMO w.f. and lies outside the aim of the present work. In this paper we simply derive AMO w.f. using SCF orbitals for the following 1st row diatomics: LiH, Li_2, HF, F_2. In all cases the splitting of doubly occupied MO's was restricted to valence shell orbitals. This involved a straightforward extension of the energy formulae given in Ref. [2] as detailed in the next section.

Construction of the AMO Wave Function

The AMO wavefunctions, we consider here, are of the form:

$$\psi = A\hat{O}_{S,M}[\psi_{\mathrm{core}}\psi_{\mathrm{val}}] \tag{1}$$

where A is the antisymmetrizer, $\hat{O}_{S,M}$ a spin projection operator and ψ_{core}, ψ_{val} are Slater determinants representing respectively a core of $2n$ electrons in n doubly occupied orbitals and a valence shell of $2m$ electrons in $2m$ singly occupied alternant molecular orbitals. Both ψ_{core} and ψ_{val} are built from a set of orthonormal orbitals $\Phi = \{\varphi_i\}$, here taken to be the SCF orbitals. As far as ψ_{val} is concerned, an occupied MO φ_i is paired to a virtual orbital $\varphi_{\bar{i}}$ to give a couple of alternant molecular orbitals u_i, v_i according to the following equation [8]

$$u_i = \cos\theta_i \varphi_i + \sin\theta_i \varphi_{\bar{i}}; \qquad v_i = \cos\theta_i \varphi_i - \sin\theta_i \varphi_{\bar{i}}. \tag{2}$$

The energy corresponding to function (1) is given by:

$$E(\psi) = E(\psi_{\text{core}}) + E(\psi_{\text{val}}) + E_{\text{int}} \tag{3}$$

where $E(\psi_{\text{core}})$, $E(\psi_{\text{val}})$ are the usual expressions for the energy of a closed shell MO and AMO wave functions respectively, and:

$$E_{\text{int}} = \sum_{i=1}^{n} \sum_{j=n+1}^{n+m} \{n_j[2(ii/jj) - (ij/ij)] + n_{\bar{j}}[2(ii/\bar{j}\bar{j}) - (i\bar{j}/i\bar{j})]\}. \tag{4}$$

In Eq. (4) n_j and $n_{\bar{j}}$ are the fractional occupation numbers of orbitals φ_j and $\varphi_{\bar{j}}$ as defined in Ref. [2]. Eqs. (3) and (4) are easily obtained by the following considerations: i) the operator $\hat{O}_{S,M}$ for $2n + 2m$ electrons appearing in Eq. (1) can be replaced by an $\hat{O}'_{S,M}$ for $2m$ electrons acting on ψ_{val} only. This property is easily proved if one remembers that the spin projection can be obtained by a suitable averaging of rotations in spin space [9] and ψ_{core} is obviously invariant under such operation; ii) ψ_{core} and ψ_{val} are strongly orthogonal because of the orthogonality of the basis Φ, and then the formulae given by McWeeny [10] for strongly orthogonal group functions can be used; iii) the density matrices of ψ_{core} and ψ_{val} are both diagonal in the basis Φ.

The last stage of the computation involves optimization of the variational parameters $\lambda_i = \cos 2\theta_i$.

Numerical Applications

SCF molecular orbitals were expressed as a linear combination of contracted gaussians centered on each atom, according to Table 1.

Orbital exponents and contraction coefficients were chosen according to Veillard [11]. A SCF procedure was performed and the resulting molecular orbitals used to build the AMO function.

The process was repeated for a number of internuclear distances for each molecule. Energies and symmetries of occupied and virtual canonical orbitals of interest are reported in Table 2. Several pairing schemes between molecular orbitals were tried; they follow the criterion of mixing orbitals having not too different energies, under the constraint that the correct spatial symmetry of the molecular wavefunction is preserved.

Energies and optimum values of variational parameters for various AMO functions are reported in Table 3. It is well known that AMO wavefunctions are equivalent to a limited C.I., where the mixing coefficients of configurations are functions of the non linear variational parameters λ_i [2]. A large number of CI-type wavefunctions have been reported in the literature for the molecules here investigated; for some of them see Ref. [13–20].

Table 1. Atomic basis set

Atom	Number of uncontracted GTO's		Number of contracted GTO's	
	s	*p*	*s*	*p*
H	6	0	2	0
Li	11	0	5	0
F	11	7	5	3

Table 2. Orbital symmetries for canonical MO SCF

Molecule and state, int. distance (a.u.)	$LiH(^1\Sigma^+)$ 3.02		$Li_2(^1\Sigma_g^+)$ 5.25		$HF(^1\Sigma^+)$1.7328		$F_2(^1\Sigma_g^+)$2.680	
	Symmetry	Energy	Symmetry	Energy	Symmetry	Energy	Symmetry	Energy
	1σ	−2.4726	$1\sigma_g$	−2.4744	1σ	−26.2963	$1\sigma_g$	−26.4364
	2σ	−0.2990	$1\sigma_u$	−2.4742	2σ	− 1.6002	$1\sigma_u$	−26.4362
	3σ	0.0109	$2\sigma_g$	−0.1845	3σ	− 0.7618	$2\sigma_g$	− 1.7745
	4σ	0.0779	$2\sigma_u$	0.0021	1π	− 0.6538	$2\sigma_u$	− 1.5020
	5σ	0.3638	$3\sigma_g$	0.0479	4σ	0.0899	$1\pi_u$	− 0.8175
			$3\sigma_u$	0.0844	5σ	0.2714	$3\sigma_g$	− 0.7463
					2π	0.2769	$1\pi_g$	− 0.6789
					6σ	0.4711	$3\sigma_u$	0.0640
					7σ	0.9954	$4\sigma_g$	0.5048
					8σ	1.6192	$4\sigma_u$	0.6207
							$2\pi_u$	0.6370
							$2\pi_g$	0.7830

Table 3. Total energies and optimum values of variational parameters λ_i (all quantities in atomic units)

Molecule and state	Int. distance	SCF Energy	AMO 2σ—3σ		AMO 2σ—4σ	
			Energy	λ	Energy	λ
LiH	2.52	— 7.9548	— 7.9553	0.949	— 7.9551	0.960
	3.02	— 7.9706	— 7.9712	0.937	— 7.9710	0.952
	3.52	— 7.9672	— 7.9682	0.920	— 7.9678	0.948
			AMO $2\sigma_g$—$2\sigma_u$		AMO $2\sigma_g$—$3\sigma_g$	
Li_2	4.50	— 14.8543	— 14.8573	0.808	—14.8545	0.894
	5.25	— 14.8614	— 14.8656	0.753	—14.8616	0.978
	6.00	— 14.8597	— 14.8660	0.678	—14.8600	0.976
			AMO 3σ—4σ			
HF	1.3328	— 99.9205	— 99.9205	1.000		
	1.7328	—100.0079	—100.0081	0.975		
	2.1328	— 99.9720	— 99.9736	0.965		
			AMO $3\sigma_g$—$3\sigma_u$			
F_2	2.267702	—198.6845	—198.7020	0.818		
	2.679718	—198.7256	—198.7814	0.600		
	3.023600	—198.6964	—198.7895	0.471		

Results

a) Li_2 *and* F_2

In both cases the most effective pairing scheme is the $(2\sigma_g - 2\sigma_u)$ which leads to a Coulson-Fischer type wave function. This splitting insures the correct limiting behaviour as the internuclear distance R approaches infinity and introduces a fraction of "left-right" correlation in the bond. For Li_2 the improvements ΔE in energy from SCF range from 0.003–0.006 a.u., which is about one half of the improvement obtained by the ODC technique [14]. Rai and Calais [4], obtained for this molecule an AMO wavefunction built from orthogonalized symmetry orbitals expressed as a linear combination of STO's of s symmetry. The improvement of the AMO energy with respect to the single determinant energy, reported by these authors is 0.017 a.u. at 6 a.u. The difference between Rai-Calais' and our results is related to the fact that they did not use SCF orbitals. In fact, by expanding each of the STO's of Rai-Calais in 4 GTO's according to the criterion of McWeeny and Huzinaga [21], we obtained the following values at $R = 6$ a.u.: -14.8504 a.u. for the $1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2$ MO wavefunction; and -14.8625 for the AMO $(2\sigma_g - 2\sigma_u)$ wavefunctions; i.e., a lowering of 0.0121 a.u. A comparison with the more refined calculations by Shukla [7] gives the same results. Similar conclusions were reached previously, on the basis of semiempirical calculations on conjugated systems [2].

The pairing scheme $2\sigma_g - 3\sigma_g$ was also tried for Li_2, as it is suggested by CI treatments [13, 16]. In this case very little improvement is obtained on the SCF function; our excited $3\sigma_g$ orbital cannot account for an effective in-out correlation in the bond. Other important mixing of orbitals would require the inclusion of π orbitals in the basis in order to allow for angular correlation.

As far as F_2 is concerned, the $3\sigma_g - 3\sigma_u$ AMO wavefunction gives satisfactorily values of ΔE: they range from 0.018 to 0.093 a.u. and compare favourably with those obtained from much more sophisticated calculations [14]. More complicate pairing schemes can be used for this molecule because of the presence of π orbitals. The following ones were tried: i) $(3\sigma_g - 3\sigma_u, 1\pi_g - 2\pi_u, 1\pi_u - 2\pi_g)$ and ii) $(3\sigma_g - 3\sigma_u, 1\pi_g - 2\pi_g, 1\pi_u - 2\pi_u)$.

In both cases mixing parameters of π orbitals were given a common value λ_π in order to ensure the correct total symmetry of the molecule. One can easily show that previous pairings lead to many determinant wavefunctions, containing configurations which have non negligible weight in some CI type wavefunctions [14] like e.g. the double excitations $1\sigma_u - 2\sigma_g$, $3\sigma_g - 3\sigma_u$ and $1\pi_g - 2\pi_u$, $3\pi_g - 3\pi_u$. The minimum was found for $\lambda_\pi = 1$, corresponding to a non-split π-orbitals.

b) LiH, HF

Results for these molecules are worse than in homonuclear cases. The only reasonable pairing scheme which introduces correlation in the bond are of the type $n\sigma - m\sigma$; they give results comparable with the $2\sigma_g - 3\sigma_g$ in homonuclear case; i.e. optimum values of λ close to 1 and small energy improvements from SCF. Numerical value of ΔE are in essential agreement with those found in an earlier split-shell calculation by Harris and Pohl [22] and smaller than those obtained by Lindner [6].

An attempt was made to improve the function by constructing the AMO's molecular orbitals from localized rather than from canonical MO's. Following the scheme of Boys and Foster [23], 2σ, 3σ and 1π were transformed in 3 equivalent lone pairs localized on F atoms and one bonding orbital l with σ-symmetry about internuclear axis. Oscillatory orbitals were than obtained from 4σ, 5σ and 2π. The AMO wavefunction was then built by pairing l with the corresponding oscillatory orbital. At the internuclear distance of 1.7328 a.u. the optimum λ is 0.980 and the energy -100.0081 a.u. Surprisingly enough no improvement in respect of the conventional AMO w.f. is obtained.

Negligible effects of this localization procedure on the AMO energy were found also in case of H_2O [24].

The computed values of the energy were used to estimate the internuclear equilibrium distances by simple parabolic interpolation. The AMO values are always larger than SCF and experimental ones, especially in the cases of Li_2 and F_2 (0.1 Å). This seems to be an indesirable consequence of the fact that the energy lowering ΔE of our calculations increases with the internuclear distance, as one can also see from Table 3. Similar behaviours have been observed in limited CI calculations [25].

As a general comment the improvement over the SCF does not seem to be very significant. AMO w.f.s comparable or even better in accuracy than the present ones were obtained using non SCF orbitals but containing adjustable parameters [4–7]. This probably means that the best orbitals for an AMO w.f. are not derivable in a simple way from the SCF ones. Analogous situations were observed in the application of the DODS scheme to atomic systems, like He [26].

Acknowledgements. The authors thank Doc. J. L. Calais and Prof. C. Zauli for stimulating discussions and critical reading of the manuscript. Financial support from CNR of Italy is gratefully acknowledged. The calculations were carried on the CDC 6600 of the Computing Centre of Bologna University.

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