Composite Wave Variational Method for Predicting Molecular Electronic Structure

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A composite wave variational method for calculating molecular orbitals has been developed and successfully applied to elementary molecules, say H_2^+, C_2, LiH, and CH_4. The good results, together with the flexibility and computational simplicity of the method, suggest that it will be a useful tool for investigating the electronic structure and related properties of complex, polyatomic molecules.

Key words: Composite wave method

Besides the method of LCAO, two more ways of approaching the study of electronic levels of molecules have been attempted, which seem to be attractive. These are the single-center expansion method by Cohen and Coulson [1] and the multiple-scattering model by Johnson [2]. In the former method, the actual molecular potential is approximated by a truncated spherical harmonic expansion and a similar expansion is used as trial function in solving numerically the Schroedinger equation. In the latter, a muffin-tin model potential is assumed and the one-electron problem is considered on the basis of a Green's function approach in the framework of the multiple-scattering approximation.

Although it was immediately realized that, due to the inherently slow convergence of the method, the single-center expansion could not be easily applied to molecules more complex than the simple class of diatomic molecules, it however shows that an accurate description of the electronic levels may be obtained only if a very close approximation of the actual molecular potential is included in the computations. For what concerns the multiple-scattering model, it enables one to introduce, at the cost of a rough description of the molecular potential, a multiple-center expansion for the trial function, thus achieving a quick convergence also in very complex molecular systems.

In the present paper we present a method which in our opinion is a compromise between the above mentioned approaches, in the sense that it makes one able to include the full molecular potential in the interatomic space, without losing the advantages deriving from a multiple-center expansion for the trial function. We account for the molecular potential in the following way: the sphero-

symmetric part of the actual potential is considered inside non overlapping spheres surrounding the nuclei; as regards the remaining space, we expand the actual potential in spherical harmonics with respect to a suitably chosen "center of the molecule".

The search of energy levels and molecular orbitals is performed within the framework of the variational principle. According to our description of the molecular potential, the trial function is built up in the following way: a linear combination of spherical harmonics, $Y_{lm}(\vartheta, \varphi)$, times energy-dependent solutions, $R_l(\varepsilon, r)$; of the radial Schroedinger equation, is considered inside the spheres; an expansion in terms of the eigenfunctions generated by the spherosymmetric part of the molecular potential with respect to the center of the molecule is instead assumed for the trial function in the remaining space. Analogously to what occurs in the APW method for solids, our trial function displays discontinuities on the surface of the spheres. For this reason the variational expression for the variational energy is written down, according to the suggestion of Schlosser and Marcus [3], as

$$
\varepsilon_v \int_{\Omega} d\Omega \psi^* \psi = \int_{\Omega_i + \Omega_0} d\Omega \psi^* H \psi + \tfrac{1}{2} \int_S dS[(\partial_n \psi_0^* + \partial_n \psi_i^*)(\psi_0 - \psi_i) - (\psi_0^* + \psi_i^*) \\
\times (\partial_n \psi_0 - \partial_n \psi_i)].
\tag{1}
$$

In the above expression Ω_i and Ω_0 denote, respectively, the regions of space inside and outside the spheres, where the trial function ψ is separately indicated by ψ_i and ψ_0. Ω denotes the whole space, S the surface of the spheres and ∂_n the outward normal derivative. H is the one-electron operator corresponding to our choice of the molecular potential and ε_v the variational energy. When expressions like

$$
\psi_i = \sum_{l,m} A_{lm} R_l(\varepsilon, r) Y_{lm}(\vartheta, \varphi)
\tag{2}
$$

for each sphere, and

$$
\psi_0 = \sum_n \sum_{l,m} B_{n,lm} R_{n,l}(r) Y_{lm}(\vartheta, \varphi)
\tag{3}
$$

for the space outside the spheres are substituted in Eq. (1) and this equation is differentiated with respect to A_{lm} and $B_{n,lm}$ according to the variational prescription, a secular equation is obtained. The whole procedure for writing down the secular equation and the numerical techniques employed for solving it are not too dissimilar from those used by Schlosser and Marcus in their APW calculation [3], apart from the fact that our basis functions in the region outside the spheres require the alpha-expansion technique [4] in evaluating the surface integrals. According to Schlosser and Marcus, a trial value is given to ε which appears in Eq. (2), and the search of each eigenvalue ε_v at which the secular determinant goes to zero, is iterated until self-consistency between ε and ε_v is reached.

The reliability of our method has first been tested on H_2^+, a molecular ion for which the energy levels are exactly known [5, 6]. Good agreement was found between the exact eigenvalues and those obtained by the present method, as it is shown on Table 1. On the same Table the values obtained by Smith and Johnson [7] on the basis of the multiple-scattering model are reported for comparison.

Table 1. Electronic energy levels of H_2^+ for the equilibrium internuclear distance $R = 2$ a.u. Energies are in Ry units

State of united atom	Exact values[a]	Scattering model[b]	Present model
$1s\sigma$	-2.20525	-2.0716	-2.2250
$2s\sigma$	-0.72174	-0.70738	-0.72184
$3s\sigma$	-0.35536	-0.34859	-0.35524
$2p\sigma$	-1.33506	-1.2868	-1.3561
$3p\sigma$	-0.51082	-0.49722	-0.49288
$4p\sigma$	-0.27462	-0.26979	-0.26262
$3d\sigma$	-0.47156	-0.45574	-0.47515
$2p\pi$	-0.85754	-0.88866	-0.84876
$3d\pi$	-0.45340	-0.44646	-0.45244

[a] Ref. [6]. – [b] Ref. [7].

Table 2. One-electron energies (in Ry) of C_2, LiH, and CH_4 for the equilibrium nuclear configuration

Molecule	Symmetry	SCF–LCAO[a,b]	Scattering model[c,d]	Present model
C_2	$2s\sigma$	-2.0567	-1.5630	-2.0321
	$3p\sigma$	-0.9662	-0.82626	-0.96988
	$3p\pi$	-0.8407	-0.85906	-0.82455
LiH	1σ	-4.8514	-4.3766	-4.8142
	2σ	-0.5972	-0.41048	-0.64472
CH_4	$1A_1$	-22.44	-21.43	-21.68
	$2A_1$	-1.88	-1.599	-1.727
	$1T_2$	-1.082	-1.024	-1.072

[a] Ref. [8]. – [b] Ref. [9]. – [c] Ref. [7]. – [d] Ref. [10].

As it appears from the Table, our method obtains in most cases the closest agreement with the exact results. In order to obtain satisfactory convergence, the secular equation was set up by including spherical harmonics up to $l = 2$ for what concerns the trial functions both inside and outside the spheres, and spherical harmonics up to $l = 4$ for what concerns the interatomic potential. As regards the time required by the whole computation, made without resorting to symmetry simplifications, it was less than 4 minutes on an IBM 360/44.

The method was then applied to multi-electron systems; on Table 2 we report the results for the one-electron energies in C_2, LiH, and CH_4. In such cases comparison is made with SCF–LCAO computations [8, 9], as well as with multiple-scattering results [7, 10]. We note that our results agree with SCF–LCAO computations better than results obtained by the multiple-scattering model, particularly in the case of C_2 where, in contrast to Smith' and Johnson's results, our method succeeds in predicting for the $p\sigma$, $p\pi$ levels the same ordering as found by Ransil's SCF–LCAO computation.

In multi-electron systems the actual one-electron potential was generated by superimposing atomic SCF charge distributions [11], and the exchange term was accounted for by Slater's approximation [12], which is known to give a rather

good agreement with Hartree-Fock one-electron energies in the case of free atoms [13]. We note that in the present work our method has been applied without requiring self consistency for the charge distribution. However it is not difficult to extend the program to a fully selfconsistent form. Preliminary results of selfconsistent computations on NH_3 [14] have shown that our method correctly predicts the inversion barrier of ammonia. This critical test has convinced us that the present method, due to its accuracy and the modest amount of computer time it requires, can be usefully applied to investigate the electronic structure and conformational properties of complex molecular systems.

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14. Antoci, S., Nardelli, G. F.: to be published

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