Theoret. chim. Acta (Berl.) 26, 351—356 (1972)

Calculations of Molecular Wave Functions in Terms of Modulated Plane Waves

M. MORANDI CECCHI
Istituto di Elaborazione dell'Informazione del C.N.R.
and Istituto di Chimica Fisica dell'Università di Pisa, Italy

O. SALVETTI
Istituto di Chimica Fisica dell'Università di Pisa, Italy

Received April 6, 1971

The possibility of representing molecular orbitals in terms of a many centre expansion of modulated plane waves is discussed. All integrals appearing in the usual SCF procedure for the calculation of the energy are obtained in an analytical form. The resulting formulae are rather simple to be evaluated.

Es wird die Möglichkeit, Molekülorbitale mittels einer Mehrzentrenentwicklung von modulierten ebenen Wellen darzustellen, diskutiert. Alle Integrale, die in einer SCF-Rechnung üblichen Typs (z. B. CNDO) erscheinen, werden in einer einfach auszuwertenden analytischen Form angegeben.

1. Introduction

The *ab initio* evaluation of accurate molecular wave functions by the Hartree-Fock method is usually approached by expanding the molecular orbitals in terms of a many-center basis set of functions referred to various atomic nuclei.

If the basis functions centered at any atom form by themselves a complete set, one may evidently get an expansion over a redundant set. When the employed number of terms at each expansion centre is small, as for example in the case of a minimal set of Slater orbitals, there is no difficulty in connection with the redundancy; as the number of terms increases, however, the overlap matrix tends to become singular the self-consistency procedure becomes more and more difficult and the loss of significant digits is such as to invalidate the results obtained. In order to obviate such difficulties, several authors, besides resorting to double or triple precision in using the computer, group the basis functions in order to get a smaller number of terms.

It is difficult, however, to formulate precise criteria to guide such procedures [1]. An expansion utilizing only a one-center complete set of basis functions does not present such difficulties, but it does not appear convenient because of the very high number of terms required. It does not have, moreover, the capability of representing discontinuities of the first derivative outside of the centre of expansion, that are required for some orbitals at certain points. A resonable way out of such difficulties appears to be the following: one should employ a small number of functions centered at the various nuclei to represent the peculiarities of the wave function in the neighbourhoods of the nuclei, and an extended set of spread-out functions to give a description of the remaining part of the wave function.

In the present research we propose to specify this idea and to obtain the set of analytical formulae useful for the SCF procedure in terms of a special type of basis functions which we will call modulated plane waves.

2. Modulated Plane Waves

The methods of evaluation previously outlined divides the molecular space into many parts. The simplest procedure would be to consider a sphere centered at the molecule center of mass with a radius such as to contain the whole molecule after assigning to each atom a volume at least equal to the Van der Waals one. In the neighbourhood of every atom, moreover, a sphere is to be of sufficiently small radius to avoid having the atoms overlap each other. The whole space is therefore divided into three regions:

The space inside the small spheres (region I), the space external to the preceeding ones but internal to the main sphere (region II), the space external to the main sphere, where the wave function essentially vanishes (region III).

However, such a subdivision would introduce considerable difficulties in the subsequent calculations, because of the continuity requirement for all molecular orbitals in every point in space. This difficulty is overcome if, instead of this partition into spheres, one replaces the above rigid spheres by proper weight functions, which we simply choose of the form e^{-r^2/l^2}. The basis functions are therefore modulated in such a way as to be unchanged in the neighbourhood of the origin, while they quickly become zero as soon as r exceeds l. The group of functions that describes the local situation in the neighbourhood of the k^{th} nucleus will be multiplied by $e^{-(r_k/l_k)^2}$, r_k being the distance from the k^{th} nucleus and l_k a parameter depending on the "dimension" of the atom considered while the spread-out functions will be multiplied by $e^{-(r/l)^2}$, with obvious meanings of the symbols. If R is the distance between two nuclei A and B and we put $l_A = l_B = \frac{R}{n}$, the two normalized weight functions overlap by $e^{-n^2/2}$, so that it is manifest that for $n = 6$ the two spaces are already practically disjoint.

We pass now to a discussion of the properties required of the basis functions. In region II, orbitals have to be represented which display neither cusp points nor very pronounced maxima that can be located *a priori*. With this object in view, it would appear convenient either to use an expansion in terms of Tchebycheff polynomials or a Fourier 3-dimensional expansion. Since the first alternative can be reduced to a linear combination of gaussian functions, in the following only the formulae are given that refer to the second kind of expansion.

As far as region I is concerned, there is no doubt that atomic orbitals of the Slater type are well suited functions, mostly owing to their capability for reproducing cusps at the nuclei. In principle such a behaviour may be obtained by means of any expansion where the r variable explicitly appears, but not by a polynomial expansion in x, y, z. On the other hand a careful description of the function at the nucleus is probably very important only in the evaluations of some particular observables (related, for instance, to the so-called Fermi contact term); but much less so for other observables, as is shown by the very good results obtained for the

energy by gaussian function expansions. For all these reasons, we have restricted our research to a Fourier 3-dimensional expansion also in the neighbourhoods of the nuclei so that in each region an expansion in terms of plane waves modulated by weight functions has been considered.

If k indicates any expansion centre, the above functions, take the form

$$\chi(l_k; \boldsymbol{r}_k) = \mathcal{N} e^{-\left((r_k/l_k)^2 + i\frac{\pi}{l_k}(\boldsymbol{n}_k \cdot \boldsymbol{r}_k)\right)}; \tag{1}$$

$\mathcal{N}$ being a normalization coefficient and $\boldsymbol{n}$ a vector with integral components. Let r be the distance of any point P from the origin 0, and r_k be the distance from a new origin 0′, and then if R is the distance between 0 and 0′, we write $\boldsymbol{N} = \boldsymbol{R} + i\frac{\pi}{l}\boldsymbol{n}$, $\alpha = 1/l_k^2$. Then (1) becomes:

$$\chi(\boldsymbol{R}, \boldsymbol{N}, \alpha; r) = \mathcal{N} e^{-\alpha r^2 + \boldsymbol{N} \cdot \boldsymbol{r}}. \tag{2}$$

3. Evaluation of Integrals

The overlap and kinetic energy integrals can easily be obtained by using the following standard integrals [2]:

$$\begin{aligned}
&\int_{-\infty}^{+\infty} e^{-px^2+qx} \mathrm{d}x = \sqrt{\frac{\pi}{p}}\, e^{q^2/4p} \\
&\int_{-\infty}^{+\infty} e^{-px^2+qx} x \mathrm{d}x = \frac{q}{2p}\sqrt{\frac{\pi}{p}}\, e^{q^2/4p} \\
&\int_{-\infty}^{+\infty} e^{-px^2+qx} x^2 \mathrm{d}x = \sqrt{\frac{\pi}{p}}\, e^{q^2/4p}\left(\frac{1}{2p} + \frac{q^2}{4p^2}\right).
\end{aligned} \tag{3}$$

In these formulae p is real and positive, while q may be complex. Thus,

$$\begin{aligned}
S &= \int \chi^*(\boldsymbol{R}, \boldsymbol{N}, \alpha; 1)\, \chi(\boldsymbol{R}', \boldsymbol{N}', \alpha'; 1)\, \mathrm{d}\tau_1 \\
&= \mathcal{N}\mathcal{N}' \int e^{-(\alpha+\alpha')r^2 + (\boldsymbol{N}^* + \boldsymbol{N}') \cdot \bar{\boldsymbol{r}}} \mathrm{d}\bar{\boldsymbol{r}} \\
&= \mathcal{N}\mathcal{N}' \int e^{-(\alpha+\alpha')x^2 + (N_x + N_x')x} \mathrm{d}x \int \ldots \mathrm{d}y \int \ldots \mathrm{d}z \\
&= \mathcal{N}\mathcal{N}' \left(\frac{\pi}{\alpha+\alpha'}\right)^{3/2} e^{\frac{(\boldsymbol{N}^* + \boldsymbol{N}')^2}{4(\alpha+\alpha')}} \\
&= \left(\frac{4\alpha\alpha'}{(\alpha+\alpha')^2}\right)^{3/4} e^{-\alpha R^2 - \alpha' R'^2 + \frac{(\boldsymbol{N}^* + \boldsymbol{N}')^2}{4(\alpha+\alpha')}}
\end{aligned}$$

$$\begin{aligned}
T &= \int \chi^*(\boldsymbol{R}, \boldsymbol{N}, \alpha; 1)\left(-\tfrac{1}{2}\nabla^2\right) \chi(\boldsymbol{R}', \boldsymbol{N}', \alpha'; 1)\, \mathrm{d}\tau \\
&= \mathcal{N}\mathcal{N}' \int e^{-(\alpha+\alpha')r^2 + (\boldsymbol{N}^* + \boldsymbol{N}) \cdot \boldsymbol{r}} (3\alpha' - \tfrac{1}{2}(\boldsymbol{N}' - 2\alpha' \boldsymbol{r})^2) \mathrm{d}\tau \\
&= \frac{\alpha\alpha'}{\alpha+\alpha'}\left(3 - \frac{\alpha\alpha'}{2(\alpha+\alpha')}\left(\frac{\boldsymbol{N}^*}{\alpha} - \frac{\boldsymbol{N}'}{\alpha'}\right)^2\right) S,
\end{aligned}$$

where $\mathcal{N} = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha R^2}$.

For the nuclear attraction integrals and for the two-electron integrals, we shall use the formulae (3) and the 3-dimensional Fourier development [3] of

$$\frac{1}{|\boldsymbol{r}_2-\boldsymbol{r}_1|}=\frac{1}{2\pi^2}\int\frac{e^{-i\boldsymbol{k}(\boldsymbol{r}_2-\boldsymbol{r}_1)}\mathrm{d}\boldsymbol{k}}{k^2}$$

that combined with the Laplace transform of $\frac{1}{k^2}$ [4]

$$\frac{1}{k^2}=\int_0^\infty e^{-tk^2}\mathrm{d}t$$

becomes

$$\frac{1}{|\boldsymbol{r}_2-\boldsymbol{r}_1|}=\frac{1}{2\pi^2}\int_0^\infty \mathrm{d}t\int e^{-tk^2-i\boldsymbol{k}(\boldsymbol{r}_2-\boldsymbol{r}_1)}\mathrm{d}\boldsymbol{k}\,.$$

If Z denotes the nuclear charge of any nucleus designated by its position vector $\boldsymbol{\varrho}$ from the origin, we have:

$$\begin{aligned}V&=-Z\int\chi^*(\boldsymbol{R},\boldsymbol{N},\alpha;1)\frac{1}{|\boldsymbol{r}-\boldsymbol{e}|}(\boldsymbol{R}',\boldsymbol{N}',\alpha';1)\mathrm{d}\tau\\&=-Z\mathcal{N}\mathcal{N}'\int e^{-(\alpha+\alpha')r^2+(\boldsymbol{N}^*+\boldsymbol{N}')\boldsymbol{r}}\frac{1}{|\boldsymbol{r}-\boldsymbol{e}|}\mathrm{d}\tau\\&=\frac{-Z\mathcal{N}\mathcal{N}'}{2\pi^2}\int e^{-tk^2-(\alpha+\alpha')r^2+(\boldsymbol{N}^*+\boldsymbol{N}'-i\boldsymbol{k})\boldsymbol{r}+i\boldsymbol{k}}\mathrm{d}t\,\mathrm{d}\boldsymbol{k}\,\mathrm{d}\boldsymbol{r}\\&=\frac{-Z\mathcal{N}\mathcal{N}'\sqrt{\pi}e^{(\boldsymbol{N}^*+\boldsymbol{N})^2/4(\alpha+\alpha')}}{(\alpha+\alpha')}\int_0^\infty\frac{e^{-(a+ib)/(\gamma+1)}}{(\gamma+1)^{3/2}}\mathrm{d}\gamma\\&=-Z(\alpha+\alpha')^{1/2}S\frac{1}{c}\operatorname{erf}(c)\,,\end{aligned}$$

where

$$a+ib=\left(\frac{\boldsymbol{N}^*+\boldsymbol{N}'}{\alpha+\alpha'}-2(\sqrt{\alpha+\alpha'})\boldsymbol{\varrho}\right)^2\quad\text{and}\quad c=\sqrt{(a+ib)}\,.$$

The two-electron integrals are calculated by the following relation:

$$\begin{aligned}I&=\int\chi^*(\boldsymbol{R}_1,\boldsymbol{N}_1,\alpha_1;1)\,\chi(\boldsymbol{R}_2,\boldsymbol{N}_2,\alpha_2;1)\frac{1}{|\boldsymbol{r}_2-\boldsymbol{r}_1|}\\&\quad\cdot\chi^*(\boldsymbol{R}_3,\boldsymbol{N}_3,\alpha_3;2)\,\chi(\boldsymbol{R}_4,\boldsymbol{N}_4,\alpha_4;2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\\&=\mathcal{N}\mathcal{N}'\int e^{-(\alpha_1+\alpha_2)r_1^2-(\alpha_3+\alpha_4)r_2^2+(\boldsymbol{N}_1^*+\boldsymbol{N}_2+i\boldsymbol{k})\boldsymbol{r}_1+(\boldsymbol{N}_3^*+\boldsymbol{N}_4-i\boldsymbol{k})\cdot\boldsymbol{r}_2}e^{-tk^2}\,\mathrm{d}t\,\mathrm{d}\boldsymbol{k}\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\\&=\frac{\pi e^{(\boldsymbol{N}_1+\boldsymbol{N}_2)^2/4(\alpha_1+\alpha_2)+(\boldsymbol{N}_3^*+\boldsymbol{N}_4)^2/4(\alpha_3-\alpha_4)}}{(\alpha_1+\alpha_2)(\alpha_3+\alpha_4)\sqrt{(\alpha_1+\alpha_2+\alpha_3+\alpha_4)}}\int_0^\infty\frac{e^{-(a+ib)/(t+1)}}{(t+1)^{3/2}}\mathrm{d}t\\&=SS'\left(\frac{(\alpha_1+\alpha_2)(\alpha_3+\alpha_4)}{\alpha_1+\alpha_2+\alpha_3+\alpha_4}\right)^{1/2}\frac{\operatorname{erf}(c)}{c}\,,\end{aligned}$$

where

$$(a+ib)=\frac{(\alpha_1+\alpha_2)(\alpha_3+\alpha_4)}{4(\alpha_1+\alpha_2+\alpha_3+\alpha_4)}\cdot\left[\frac{N_1^*+N_2}{\alpha_1+\alpha_2}-\frac{N_3^*+N_4}{\alpha_3+\alpha_4}\right]^2$$

$$c=\sqrt{a+ib}$$

and S and S' are the overlap integrals between the first and the second pair of functions.

The actual utilization of the preceding expressions offers some difficulties only in as far as the calculation of the function erf(z) when z is complex [5a] is concerned. That is, numerical problems arise when $|z|$ is not a small quantity, because in such a case the Maclaurin series development is not convenient any more [6]. In order to overcome this trouble, it was found convenient to put $z=x+iy$ and to use the following expressions:

$$\operatorname{erf}(z)=1+\varepsilon \quad \text{for} \quad x^2-y^2>17, \quad \text{where} \quad |\varepsilon|<4\cdot 10^{-8}$$

$$\operatorname{erf}(z)=\frac{i\,2e^{y^2}}{\sqrt{\pi}}F(y) \quad \text{for} \quad x=0$$

$$\operatorname{erf}(z)=1-\frac{2}{\sqrt{\pi}}e^{-2ixy}\int_1^\infty e^{-x^2t^2+y^2/t^2}(x-iy/t^2)\,\mathrm{d}t, \tag{4}$$

$$\operatorname{erf}(z)=\operatorname{erf}(x)+\frac{i\,2e^{-x^2}}{\sqrt{\pi}}\int_0^y e^{t^2+2itx}\,\mathrm{d}t, \tag{5}$$

$$\operatorname{erf}(z)=\frac{i\,2e^{y^2}}{\sqrt{\pi}}F(y)+\frac{2e^{y^2}}{\sqrt{\pi}}\int_0^x e^{-(t^2+2ity)}\,\mathrm{d}t, \tag{6}$$

where $F(y)=e^{-y^2}\int_0^y e^{t^2}\,\mathrm{d}t$ is the Dawson's function [5a] for which $0\leqq F(y)\leqq 0.54104422$.

The use of the expression (5) is the more convenient when y is small with respect to x, while the expression (6) is instead more convenient when x is small with respect to y.

In order to evaluate the integral appearing in (4), we pose:

$$\int_1^\infty e^{-x^2t^2+y^2/t^2}(x-iy/t^2)\,\mathrm{d}t\simeq\int_1^u e^{-x^2t^2+y^2/t^2}(x-iy/t^2)\,\mathrm{d}t, \tag{7}$$

where

$$u=\sqrt{\frac{x^2-y^2+17}{2x^2}+\sqrt{\left[\frac{y^2-x^2-17}{2x^2}\right]^2+\frac{y^2}{x^2}}}.$$

The integrals which appear in the expressions (5), (6) and (7) may be easily evaluated numerically with a relatively few Gauss points.

References

1. Clementi, E., Davis, D. R.: J. chem. Physics **45**, 2593 (1966); Ritchie, C. D., King, H. F.: J. chem. Physics **47**, 565 (1967); Newman, D., Moskowitz, J. W.: J. chem. Physics **49**, 2056 (1968).
2. Gradshteyn, I. S., Ryzhik, I. M.: $\Sigma\pi\int$ Tables, p. 146. Berlin: VEB Deutscher Verlag der Wissenschaften 1957.
3. Carrier, G. F., Krook, M., Pearson, C. E.: Functions of a complex variable. McGraw-Hill Book Company 1965.
4. Widder, D. V.: The Laplace transform. Princeton University Press 1946.
5. Abramowitz, M., Stegun, I. A.: Handbook of mathematical functions, a) p. 297, b) p. 298. New York: Dover Publications Inc. 1965.
6. Salzer, H. E.: Formulas for calculating the error function of a complex variable. Math. Tables Aid Comp. **5**, 67–70 (1951).

Dr. M. Morandi Cecchi
Istituto di Chimica Fisica
Università di Pisa
Pisa, Italy