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David M. Bishop

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## Use of Fock-Petrashen and Hydrogenic Orbitals in Single-Center Wavefunctions

DAVID M. BISHOP

Chemistry Department, University of Ottawa, Canada

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The use of Fock-Petrashen, Slater, and hydrogenic orbitals within the single-center method is studied and compared for a single determinantal wavefunction of  $H_2O$ . The use of Slater orbitals is found to be superior and the reasons for this are given.

## 1. INTRODUCTION

THE mathematical difficulties of solving the non-relativistic Schrödinger equation for molecules with a fixed nuclear framework have led theoreticians to look for approximate solutions. One approach has been to consider the total electronic wavefunction to be composed of one-electron atomic orbitals centered at a single point in space (the single-center method), and then to use the variational theorem to determine the "best" wavefunction of the form chosen. Within the single-center method there are many choices for the form of the atomic orbitals and in this paper three types of orbital are discussed and compared: Schmidt orthogonalized Slater orbitals (SS), Fock-Petrashen orbitals (FP), and hydrogenic orbitals (H).

FP orbitals<sup>1</sup> were first used in the single-center method by Bernal<sup>2</sup> and more recently by Gaspar *et al.*<sup>3</sup> and by Banyard and Hake<sup>4</sup>; the first three orbitals of this type have the following form (normalization factors are omitted):

$$\begin{aligned} 1s &\sim \exp(-\alpha r), \\ 2s &\sim [1 - (\alpha + \beta)r/3] \exp(-\beta r), \\ 2p_z &\sim r \exp(-\gamma r) \cos\theta, \end{aligned} \quad (1)$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  are variable exponents chosen such as to minimize the total energy, and  $r$  and  $\theta$  are the electronic coordinates, usually centered on the heavy nucleus. It is seen that the  $1s$  and  $2s$  orbitals are mutually orthogonal.

Slater-type orbitals have been used by Bishop *et al.*,<sup>5</sup> among others, and have usually been orthogonalized by the Schmidt procedure; this orthogonalization makes

no difference to the final result but does simplify the mathematics as well as allowing for a direct comparison with the orbitals of Eqs. (1). The first three SS orbitals are then of the form

$$\begin{aligned} 1s &\sim \exp(-\alpha r), \\ 2s &\sim r \exp(-\beta r) - 24\alpha^3 \exp(-\alpha r)/(\alpha + \beta)^4, \\ 2p_z &\sim r \exp(-\gamma r) \cos\theta, \end{aligned} \quad (2)$$

and  $\alpha$ ,  $\beta$ , and  $\gamma$  are once again variable exponents.

The first three hydrogenic orbitals are of the same form as those in Eqs. (1) except that  $\beta$  is fixed as  $\alpha/2$ . These orbitals have been used in single-center calculations by Funabashi and Magee<sup>6</sup> and they are

$$\begin{aligned} 1s &\sim \exp(-\alpha r), \\ 2s &\sim (2 - \alpha r) \exp(-\alpha r/2), \\ 2p_z &\sim r \exp(-\gamma r) \cos\theta. \end{aligned} \quad (3)$$

A more general set of orbitals can be formed such as to include these three types as special cases, i.e.,

$$\begin{aligned} 1s &\sim \exp(-\alpha r), \\ 2s &\sim (r - a) \exp[-\beta(r - a)] + b \exp[-\alpha(r - a)], \\ 2p_z &\sim r \exp(-\gamma r) \cos\theta. \end{aligned} \quad (4)$$

The orthogonalization condition,

$$\int 1s2s d\tau = 0,$$

gives the requirement that

$$b = [a - 3/(\alpha + \beta)][2\alpha/(\alpha + \beta)]^3 \exp[a(\beta - \alpha)].$$

It can be seen that when  $a=0$ , Eqs. (2) result; when  $a=3/(\alpha + \beta)$ , Eqs. (1) result; and when  $a=2/\alpha$  and  $\beta=\alpha/2$ , Eqs. (3) are produced. Use of FP, SS, or H

<sup>1</sup> V. Fock and M. J. Petrashen, *Physik. Z. Sowjetunion* **6**, 368 (1934); **8**, 359 (1935).

<sup>2</sup> M. J. M. Bernal, *Proc. Phys. Soc. (London)* **A66**, 514 (1953).

<sup>3</sup> R. Gaspar, I. Tamassy-Lentei, and Y. A. Krugylak, *J. Chem. Phys.* **36**, 740 (1962).

<sup>4</sup> K. E. Banyard and R. B. Hake, *J. Chem. Phys.* **41**, 3221 (1964).

<sup>5</sup> D. M. Bishop, J. R. Hoyland, and R. G. Parr, *Mol. Phys.* **6**, 467 (1963).

<sup>6</sup> K. Funabashi and J. L. Magee, *J. Chem. Phys.* **26**, 407 (1957).

TABLE I. Parameters and total energy for H<sub>2</sub>O.

	Calculation (1) FP orbitals	Calculation (2) SS orbitals	Calculation (3) H orbitals	Calculation (4) General	FP orbitals <sup>a</sup>	H orbitals <sup>b</sup>
$R_{OH}$ (a.u.)	1.81	1.81	1.81	1.81	1.81	1.80
HOH	105°	105°	105°	105°	105°	105°
$\alpha$	7.716	7.667	7.191	7.669	7.67	7.165
$\beta$	2.626	2.136	...	2.154	2.63	...
$\gamma$	1.884	1.901	1.756	1.901	1.885	1.791
$a^c$	(0.290)	(0.0)	(0.278)	0.0156	...	...
$E$ (a.u.)	-75.0064	-75.1948	-74.1605	-75.1950	-75.00	-73.80

<sup>a</sup> K. E. Banyard and N. H. March, Acta Cryst. 9, 385 (1956).<sup>b</sup> Reference 6.<sup>c</sup>  $a$  is only an independent variable for Calculation (4); in the first three calculations it is, respectively,  $3/(\alpha+\beta)$ , 0.0, and  $2/\alpha$ .

orbitals is therefore a restriction, to some extent, of the more general form, Eqs. (4), and the question is: Which restriction retains most flexibility and gives the lowest energy for a particular molecule when, say, only a single determinantal wavefunction is used? The answer to this question is the purpose of the present paper, and the answer is found by treating the H<sub>2</sub>O molecule using each of the four sets of orbitals.

## 2. CALCULATION AND RESULTS

We require, therefore, the ground-state energy and the total wavefunction for the water molecule within the single-center method using the four sets of orbitals, Eqs. (1)–(4). We form  $\Psi$ , the total wavefunction, as a 10-electron Slater determinant, i.e.,

$$\Psi = (10!)^{-1/2} | 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 |,$$

and minimize the total molecular energy,

$$E = \int \Psi^* \mathcal{H} \Psi d\tau / \int \Psi^* \Psi d\tau,$$

through the variable parameters. Adopting the Born-Oppenheimer approximation, we can write the total Hamiltonian operator as

$$\mathcal{H} = \sum_i \left[ -\frac{1}{2} \nabla_i^2 - 8/r_i - \sum_{\alpha} (r_{\alpha i})^{-1} \right] + \sum_{i < j} (r_{ij})^{-1} + 16/R + 1/R_{12}.$$

The indices  $i$  and  $j$  extend over the 10 electrons and  $\alpha$  over the two protons. The distances  $r_i$ ,  $r_{\alpha i}$ ,  $r_{ij}$ ,  $R$ , and  $R_{12}$  are, respectively, oxygen–electron, proton–electron, electron–electron, oxygen–proton, and proton–proton. The coordinate system is centered on the oxygen nucleus.

It is straightforward to evaluate  $E$  as a function of the molecular geometry and the variable parameters and for the details of this the reader is referred to Ref. 5. Four calculations are now made for the four sets of orbitals and their concomitant restrictions. In each case the bond distance and angle are taken as

1.81 a.u. and 105°, respectively, and the exponents of the three  $2p$  orbitals are taken to be the same,  $\gamma$ , producing a wavefunction  $\Psi$  which is spherically symmetric. Integer principle quantum numbers have been used in all calculations and atomic units (1 a.u. of length = 0.52915 Å, 1 a.u. of energy = 27.210 eV) also used throughout. The variable parameters such as to minimize the total energy were chosen by the "Pattern Search Method."

For Calculation (1) using the FP orbitals, Eqs. (1), there were three variables,  $\alpha$ ,  $\beta$ , and  $\gamma$ , and likewise for Calculation (2) using the SS orbitals of Eqs. (2). For Calculation (3), using the H orbitals, Eqs. (3), there were only two variables,  $\alpha$  and  $\gamma$ ; and for Calculation (4), using the general orbitals, Eqs. (4), there were four variables,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $a$ . In Table I the

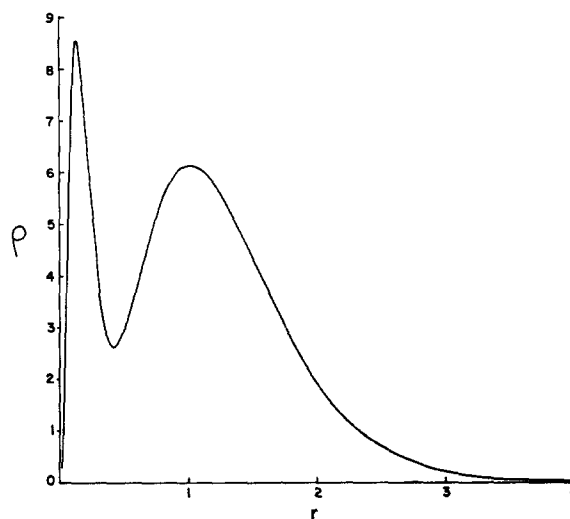


FIG. 1. Electron radial distribution function,

$$\rho = \int_0^{2\pi} \int_0^\pi \Psi^* \Psi r^2 d\theta d\phi,$$

against distance,  $r$  (in atomic units), for H<sub>2</sub>O, Calculation (4).

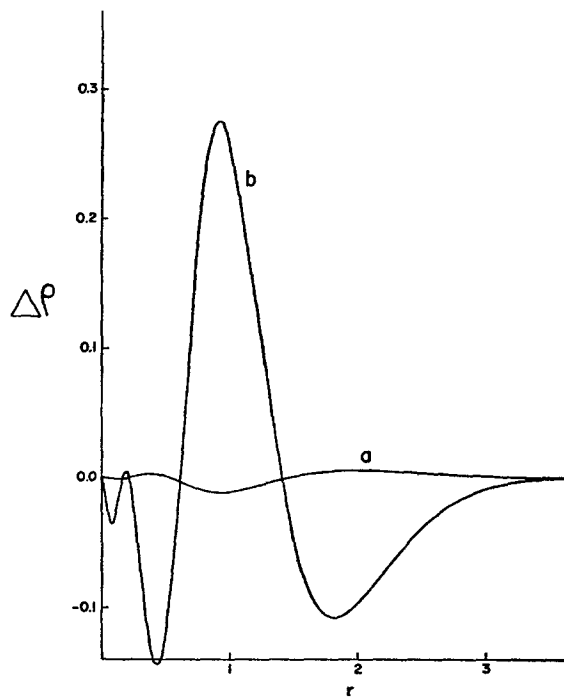


FIG. 2. Curve a: Difference between  $\rho$  for Calculations (2) and (4),  $\Delta\rho$ , against distance,  $r$  (in atomic units). Curve b: Difference between  $\rho$  for Calculations (1) and (4),  $\Delta\rho$ , against distance,  $r$  (in atomic units).

results of these four calculations are given and, for comparison, in the last two columns, the results of earlier work. The electron radial distribution function

$$\rho = \int_0^{2\pi} \int_0^\pi \Psi^* \Psi r^2 d\theta d\phi, \quad \int_0^\infty \rho dr = 10,$$

is plotted in Fig. 1 for Calculation (4) and the difference between this distribution and that for Calculations

(1) and (2) is given in Fig. 2; the difference for Calculation (3) is not plotted, but it is an order of magnitude greater than the difference for Calculation (2).

### 3. DISCUSSION

From Table I it is seen that the optimum value of  $a$  (0.0156) is much closer to zero than to the FP value (0.290); the results of using SS orbitals are therefore closer to the general calculation and much superior to either FP or H results. The energy improvement in using SS orbitals over FP orbitals is about 0.2 a.u. The plots of electron radial distribution functions are even more striking, the SS wavefunction very closely follows the general wavefunction, whereas the FP results are comparatively poor.

The  $2s$  function of Eqs. (4) can be obtained from the SS  $2s$  function by the addition of a second  $1s$  orbital whose exponent is  $\beta$ , so the results also give the information that such an addition leads to an insignificant energy decrement (0.0002 a.u.).

The conclusion, therefore, is that the use of FP orbitals is always likely to lead to inferior results compared with SS orbitals and that the use of hydrogenic functions will give even poorer results as these orbitals are even more restricted than the FP orbitals. This conclusion will not necessarily hold, however, if a multi-determinantal form is used for  $\Psi$ . It is always possible to make up for the deficiencies in orbitals by using a great number of them, but this is wasteful when the better orbitals, SS, are as easy to handle.

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