

for  $Y(\beta, n)$  to find its value for a large  $n$  and compared it with the value predicted by recursion.

Almost all matrices encountered were symmetric. This property was used as a check in the initial phases of each machine computation.

The most powerful check was the following. We

chose  $f_i(\frac{1}{2}\sigma t) = \cosh(\frac{1}{2}\sigma t)$ , took  $\sigma=0$ , and picked  $p_i, q_i, r_i$  so that we had functions suitable for the ground state. By setting  $\sigma=0$  in our programs we tabulated functions, integrals, and matrices for this state. All energy corrections were then calculated and compared with published results.

## Analytic Hartree-Fock Solutions for $O^{\dagger}$

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$O^{\dagger}$  ions exist in solids but not in a free state. Analytic Hartree-Fock solutions have been obtained for the  ${}^1S$  state of  $O^{\dagger}$  which can be applied to work in solids. The solutions utilize stabilizing potential wells of positive charge and the results are compared with other published work.

### INTRODUCTION

A NUMBER of the oxide crystals are of interest because of their magnetic properties. They are ionic in nature, their oxygens having double negative charges. Because of this, it seemed desirable to obtain  ${}^1S(1s)^2(2s)^2(2p)^6 O^{\dagger}$  wave functions of a form which might be useful in discussions of the properties of the solids. No one has experimentally observed free  $O^{\dagger}$  ions. It is doubtful that a Hartree-Fock solution, which is a single determinant s.c.f. (self-consistent field) calculation, would converge to a state with all ten electrons bound for a free  $O^{\dagger}$ . Crystalline  $O^{\dagger}$  ions are stabilized by their environment and because of this it is reasonable both to talk of  $O^{\dagger}$  ions in crystals and to hope to get meaningful single determinant  $O^{\dagger}$  solutions for further work in solids. It was decided to do analytic Hartree-Fock calculations using stabilizing potential wells which are described below.

### PROCEDURE

The technique used was the Roothaan procedure<sup>1</sup> as modified by Nesbet<sup>2</sup> for use on the Whirlwind digital

computer at M.I.T. In this method, one starts with a set of one-electron basis functions of the form

$$\eta_i(l, m) = r^{A_i+l} e^{-Z_i r} Y_l^m(\theta, \phi).$$

An s.c.f. calculation is then done, subject to the limitations imposed by the choice of the set of  $\eta_i$ 's. A final set of orthonormal one-electron functions results with each function having the form

$$\psi_j(l, m) = \sum_i C_{ji} \eta_i(l, m),$$

where the summation is over all  $\eta_i$ 's with the  $l$  and  $m$  values of the  $\psi_j$  in question. The computer programs had the facility for adding potentials due to charged environments other than and in addition to the nuclear potential. In the calculations described here, a sphere of uniform positive charge was added. Such a sphere causes a discontinuity in electric field rather than in potential at the sphere radius giving us a "shouldered" instead of square-well potential.

At first, a set of wells was used whose radii were equal to the nearest-neighbor distances in several of the oxides and whose charge gave the wells a depth equal to the Madelung potential. Such a choice was not at all satisfactory since it did not include the nearest-neighbor electronic repulsion. Professor Slater

TABLE I. Parameters of the basis functions ( $\eta_i$ 's).

$i$	$l$	$A_i$	$Z_i$
1	0	0	7.700
2	0	1	1.490
3	0	1	2.803
4	0	1	1.776
5	1	0	0.714
6	1	0	3.412
7	1	0	1.384

TABLE II. Analytic form of the wave functions.

+1 Well solution	
$\psi_{(1s)}$	$= 42.30203\eta_1 + 0.19342\eta_2 + 0.85427\eta_3 - 0.47313\eta_4$
$\psi_{(2s)}$	$= -10.38130\eta_1 + 0.13332\eta_2 + 6.21035\eta_3 + 2.94794\eta_4$
$\psi_{(2p)}$	$= 0.11617\eta_5 + 8.74998\eta_6 + 1.49205\eta_7$
+2 Well solution	
$\psi_{(1s)}$	$= 42.30129\eta_1 + 0.19240\eta_2 + 0.85365\eta_3 - 0.47105\eta_4$
$\psi_{(2s)}$	$= -10.24975\eta_1 + 0.16271\eta_2 + 5.97706\eta_3 + 2.97325\eta_4$
$\psi_{(2p)}$	$= 0.07800\eta_5 + 8.51793\eta_6 + 1.66494\eta_7$

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<sup>1</sup> C. C. J. Roothaan, *Revs. Modern Phys.* **23**, 69 (1951).

<sup>2</sup> R. K. Nesbet, *Proc. Roy. Soc. (London)* **A230**, 312 (1955).

suggested another well based on the following argument: consider the potential energy that one electron sees due to the nuclear charge of +8 and the other nine electrons. At the nucleus the potential energy has gone to  $-\infty$  and as the electron moves out radially, the potential energy increases, goes through a maximum and then drops off slowly due to the net charge of  $-1$  of the rest of the ion. A sphere of charge  $+1$  at the maximum would destroy the repulsion for large  $r$  while leaving the "correct" potential for the interior. In many atomic calculations, there is included a tabulation of the total charge within a radius  $r$  as a function of  $r$ . Hartree<sup>3</sup> has published this for Cl<sup>-</sup> and it can be

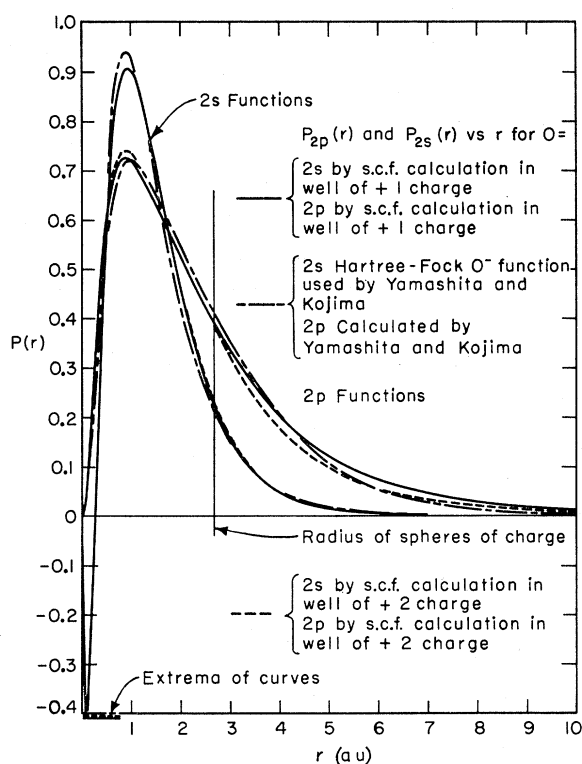


FIG. 1.  $P_{2p}(r)$  and  $P_{2s}(r)$  vs  $r$  (in atomic units) for O<sup>-</sup>.

seen that the neutral-charge radius comes at about the commonly tabulated ionic radius. It was decided to use the O<sup>-</sup> ionic radius for the sphere of charge. There is some disagreement as to what its value is. In this work, the most common value of 1.40 Å or 2.66 au (atomic units) was chosen.

Argument for using a stabilizing well of  $+2$  charge can be made since the net charge produced by the remainder of a crystal would be just that. The results presented in this paper describe the  $+1$  well calculation fully but also give the wave functions resulting from a  $+2$  well calculation, with the same radius, involving the same  $\eta_i$ 's.

<sup>3</sup> D. R. Hartree, Proc. Roy. Soc. (London) A141, 282 (1933).

TABLE III. One-electron energies, well potential energies, and nuclear potential plus kinetic energies for the  $+1$  well solution. Values in Rydbergs.

One-electron energies (including well potential)	Well potential energies	Nuclear potential plus kinetic energies
$\mathcal{H}_{1s} = -40.315872$	$V_{1s} = -0.763908$	$K_{1s} = -63.832428$
$\mathcal{H}_{2s} = -1.573926$	$V_{2s} = -0.761838$	$K_{2s} = -13.516988$
$\mathcal{H}_{2p} = -0.160166$	$V_{2p} = -0.736926$	$K_{2p} = -10.887736$

## RESULTS

Table I gives the values of the  $\eta_i$  parameters for the reported calculations. One  $\eta_i$  was supplied for the  $1s$  function ( $l=A_i=0$ ) and this was also used for the inner loop of the  $2s$  function. Three  $\eta_i$ 's were supplied for the outer loop of the  $2s$  function ( $l=0, A_i=1$ ) and three were also used for the  $2p$  function ( $l=1, A_i=1$ ). A series of calculations was done varying the  $Z_i$ 's in order to obtain a best set. A number of applications of the method of steepest descents were made. The criterion was the minimization of the total ionic energy (including the well). The number of parameters and their interdependent effects on the energy made systematic parameter variation very difficult and as a result there is some uncertainty as to how close the results are to the best possible energy for seven  $\eta_i$ 's. The author believes that the energy differs from such a best possible energy by no more than 0.02 Rydberg or slightly more than 0.01% of the total energy. Energy can be improved by adding more  $\eta_i$ 's and in fact a calculation was done with an extra  $2p$   $\eta$  giving an improvement of 0.024 Rydberg. Adding  $\eta_i$ 's is undesirable since it makes the final function more cumbersome for use in solid-state work.

Table II gives the wave functions for the two wells in their analytic form and the  $2s$  and  $2p$  functions are plotted in Fig. 1 along with the results of Yamashita and Kojima.<sup>4</sup> The one-electron energies ( $\mathcal{H}$ ), the well potential energies ( $V$ ), and the nuclear potential plus kinetic energies ( $K$ ) are presented in Table III for the  $+1$  well solution. The one-electron energies include the well potentials. In Table IV the two-electron integrals for the  $+1$  well are given in the form of  $G^k$  and  $F^k$  integrals as defined by Condon and Shortley.<sup>5</sup> Table V

TABLE IV. Two-electron  $F^k$  and  $G^k$  integrals for the  $+1$  well solution, in Rydbergs.

$F^0(1s,1s) = 9.494122$	$G^1(1s,21) = 0.139619$
$F^0(2s,2s) = 1.490274$	$G^1(2s,2p) = 0.755039$
$F^0(2p,2p) = 1.153652$	$F^0(1s,2s) = 2.158288$
$F^2(2p,2p) = 0.478903$	$F^0(1s,21) = 1.792862$
$G^0(1s,2s) = 0.147794$	$F^0(2s,2p) = 1.300147$

<sup>4</sup> J. Yamashita and M. Kojima, J. Phys. Soc. (Japan) 7, 261 (1952).

<sup>5</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1953), in particular, p. 177.

TABLE V. Energy relations.

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$$\begin{aligned} \mathcal{H}C_{1s} &= K_{1s} + V_{1s} + F^0(1s,1s) + 2F^0(1s,2s) \\ &\quad - G^0(1s,2s) + 6F^0(1s,2p) - G^1(1s,2p) \\ \mathcal{H}C_{2s} &= K_{2s} + V_{2s} + 2F^0(1s,2s) - G^0(1s,2s) \\ &\quad + F^0(2s,2s) + 6F^0(2s,2p) - G^1(2s,2p) \\ \mathcal{H}C_{2p} &= K_{2p} + V_{2p} + 2F^0(1s,2p) - \frac{1}{3}G^1(1s,2p) + 2F^0(2s,2p) \\ &\quad - \frac{1}{3}G^1(2s,2p) + 5F^0(2p,2p) - \frac{2}{3}F^2(2p,2p) \end{aligned}$$

$$\begin{aligned} \text{Total energy} &= \sum_i^{\text{all electrons}} \frac{1}{2}(V_i + K_i + \mathcal{H}C_i) \\ &= 2K_{1s} + 2K_{2s} + 6K_{2p} + 2V_{1s} + 2V_{2s} + 6V_{2p} \\ &\quad + F^0(1s,1s) + F^0(2s,2s) + 15F^0(2p,2p) \\ &\quad - (6/5)F^2(2p,2p) + 4F^0(1s,2s) \\ &\quad - 2G^0(1s,2s) + 12F^0(1s,2p) + 12F^0(2s,2p) \\ &\quad - 2G^1(1s,2p) - 2G^1(2s,2p) \end{aligned}$$


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expresses the  $\mathcal{H}C$ 's in terms of the other integrals and gives the expression for the total energy. The total ionic energy (including well energy) was  $-156.1194$  Rydbergs for the  $+1$  well and  $-163.4968$  Rydbergs for the  $+2$  well.

Yamashita and Kojima took  $1s$  and  $2s$  functions from an existing Hartree-Fock solution<sup>6</sup> for  $O^-$  and calculated an analytic  $2p$  function variationally. They used two  $2p$   $\eta$ 's and their stabilizing environment consisted of six  $Mg^{++}$  ions at the  $MgO$  nearest-neighbor

distance. Gaspar and Csavinszky<sup>7</sup> also have obtained  $O^-$  solutions but they used a single exponential for the  $2p$  function and the author believes that this is a severe limitation.

Wave functions outside of the radii of the spheres of charge (= ionic radius) are of little interest since this is just the region in a solid where the atomic description of  $O^-$  breaks down. In the "inner" region, the  $+1$  and  $+2$  well solutions have the same general form. The author obtained solutions for other and violently different wells and was impressed by how insensitive the "inner" part of the functions are to environment. There is greater difference between the author's and Yamashita and Kojima's results. The maxima of the author's  $2p$  functions lie inside and the  $2s$  outside of theirs. The way the  $2s$  and  $2p$  functions shift to compensate each other suggests that the difference in results is primarily due to their not obtaining a  $2s$  function variationally.

#### ACKNOWLEDGMENTS

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<sup>6</sup> Hartree, Hartree, and Swirles, *Trans. Roy. Soc. (London)*, **238**, 229 (1939).

<sup>7</sup> R. Gaspar and P. Csavinszky, *Acta Phys. Acad. Sci. Hung.* **4**, 125 (1956).