

## Hartree-Fock Calculations for $Mn^{++}$ in Cubic Fields\*

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Hartree-Fock calculations have been carried out for the  $Mn^{++}$  ion in cubic fields produced by sets of octahedrally placed point charges. The two types of cubic  $3d$  electrons were allowed to have different radial dependence. The relaxation of the constraint of having a single  $3d$  radial function led to effects which were small but which the writer believes should be included in any detailed treatment of a paramagnetic ion in a crystalline field.

### I. INTRODUCTION

ATTEMPTS at parameterizing experimental optical absorption data have been met with a great deal of success. A number of different sets of parameters have been used. One that has been frequently used when studying data for iron series (Sc to Cu) ions in cubic fields is  $F^2(3d,3d)$ ,  $F^4(3d,3d)$ , and  $D_q$ . The  $F^k(3d,3d)$ 's are Slater two-electron integrals and  $D_q$  measures the interaction between the ion and the crystalline field. There are several important assumptions behind this choice of parameters. First, it is assumed that the iron series ion can be described as a Hartree-Fock wave function. Secondly, that for any state of the ion, there is a common one-electron radial function for all the electrons in any given shell and lastly, that all the ion states have a common one-electron radial function for each shell. Work has been done in trying to make theoretical predictions of the parameters and the results have been poor. It has often been the case that the cruder efforts have led to the best results.

This paper is primarily concerned with the prediction of  $D_q$ 's but let us first consider  $F^2(3d,3d)$  and  $F^4(3d,3d)$  and in particular turn to  $F^k(3d,3d)$ 's for free iron series atoms and ions. The  $F^k(3d,3d)$ 's appear as parameters in the multiplet spectra if the assumptions of the last paragraph are made. Much work has been done in fitting parameters to the experimental multiplet spectra. This work has been only mildly successful. Difficulties frequently occur when attempting to predict the energy difference between states of different total atomic spin ( $S$ ). For example,<sup>1</sup> the  $(3d)^3$  configuration has sextet, quartet and doublet states and several of the doublets are violently out of position for any choice of the  $F^k(3d,3d)$ 's which give reasonable positions for the other states. We should note that occasionally there have been difficulties in parameterizing optical absorption data when the resonance has involved transitions between states of differing  $S$ . It has been generally thought that this was due to spin dependent

$D_q$ 's. The free ion fits suggest that there are other possible causes for this.

The writer<sup>1,2</sup> has done a number of Hartree-Fock calculations for the iron series atoms and ions. The resultant  $F^k(3d,3d)$ 's predict more widely spaced multiplet spectra than are observed. In other words, the calculated  $F^k(3d,3d)$ 's are larger than the "experimental"  $F^k(3d,3d)$ 's. Accurate predictions of the observed free ion spectra require the handling of the "correlation" problem and the abandonment of the one-electron function, one radial function per shell, Hartree-Fock description of an ion. This implies that the "experimental"  $F^k(3d,3d)$ 's should not be thought of as exact  $F^k(3d,3d)$  integrals. Due to the absence of the exchange interaction between electrons, Hartree calculations yield one-electron wave functions which are expanded in comparison with Hartree-Fock functions. As a result, the Hartree  $F^k(3d,3d)$ 's are smaller and in better agreement with the "experimental"  $F^k(3d,3d)$ 's. One might think that the smaller  $F^k(3d,3d)$ 's give us a reason for using Hartree rather than Hartree-Fock wave functions. The writer does not agree with this for he dislikes the technique of using a cruder formalism for which errors happen to cancel and, as we will see shortly, the extended nature of Hartree functions can give trouble when one computes  $D_q$ 's. In contrast with a Hartree solution, a treatment of the "correlation" problem (for example through the use of configuration interaction) will lead to an electronic charge density which is contracted in comparison with a Hartree-Fock charge density.

Let us now consider the problem of predicting  $D_q$  values for the optical absorption of iron series ions. To do this we need a  $3d$  one-electron radial function and a cubic field. With these we have

$$D_q \sim \int_0^\infty [u_{3d}(r)]^2 V_4(r) dr, \quad (1)$$

where  $u_{3d}(r)/r$  is the radial part of the  $3d$  wave function ( $\psi_{3d}$ ) and  $V_4(r)$  gives the dependence of the cubic field on the distance ( $r$ ) from the iron series ion. One would like to obtain the  $3d$  function by a self-consistent field calculation for the ion inside an appropriate potential. No such calculations have existed and in fact until

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<sup>1</sup> R. E. Watson, Iron Series Hartree-Fock Calculations, Technical Report No. 12, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, June 15, 1959 (unpublished).

<sup>2</sup> R. E. Watson (to be published).

recently,<sup>3</sup> no truly self-consistent Hartree-Fock calculation has existed for a free, unclosed  $3d$  shell, iron series ion. As a result, workers have used Hartree or even cruder functions. The  $V_4(r)$ 's which have been used have generally been even more crudely based. To illustrate this, let us consider the case of an iron series ion surrounded by an octahedral array of six nearest neighbor negatively charged ions. Such a situation occurs on the insertion of an iron series ion into an ionic NaCl structure crystal. The simplest model for the crystalline field is one where the nearest neighbor ions are treated as point charges and the rest of the crystal is neglected. The resultant  $V_4(r)$  is illustrated in Fig. 1 for neighboring ion charges of  $-1$  and  $-2$ . A somewhat more realistic environment would be one where the point charges are replaced by the free ion charge densities. This would give a  $V_4(r)$  of the form also illustrated in Fig. 1. This  $V_4(r)$  has some interesting features. As one moves out from the iron series ion (the origin),  $V_4(r)$  is small and positive and then it becomes large and negative in the region of the nearest neighbor ions. This is easily understood, for we can draw a sphere about a nearest neighbor ion such that the total charge inside the sphere is zero. Outside of the sphere the ion's charge appears to be negative [and hence  $V_4(r)$  is positive for a negatively charged electron] and inside the sphere the ion appears to be positively charged [with  $V_4(r)$  negative]. This means that there is a region where the integrand of Eq. (1) contributes positively to  $D_q$  and another region where a negative contribution is made. This can cause difficulties as Kleiner's<sup>4</sup> work shows. Kleiner used a similar  $V_4(r)$  in a crystalline field calculation for chrome alum. Six  $H_2O$  molecules form an octagon about a  $Cr^{+++}$  ion in this substance. A  $3d$  function from a Hartree calculation by Mooney<sup>5</sup> for  $Cr^{++}$  was used and a negative  $D_q$  was obtained. This is the wrong sign. The author's more recent H-F calculations<sup>1,2</sup> for  $Cr^{++}$  (the ion for which

Mooney made his calculation) and  $Cr^{+++}$  (the ion in chrome alum) yield  $3d$  functions which are more contracted than Mooney's function. Either of the author's  $3d$  functions would yield a positive  $D_q$  when integrated with Kleiner's  $V_4(r)$ . A calculation with the cruder point charge  $V_4(r)$  would have, of necessity, yielded a positive  $D_q$ . Kleiner's experience is illustrative of the problems connected with a calculation for a  $D_q$ .

It is clear that the choice of  $3d$  functions and  $V_4(r)$ 's is critical. This matter has not been extensively explored due to the computational difficulties associated with the work. The purpose of this paper is to investigate the choice of  $3d$  functions with particular emphasis on the question of whether or not it is reasonable to restrict the  $3d$  electrons to a single radial function. The choice of  $V_4(r)$ 's will not be investigated. The writer has attempted to gain insight into these matters with a series of Hartree-Fock calculations for the  $Mn^{++}$  ion in a cubic field due to a set of six octahedrally placed point charges. Point charge  $V_4(r)$ 's were used because they could be handled with existing Hartree-Fock procedure computer programs. The "strong field" approximation was used (i.e., the individual  $3d$  one-electron functions have cubic symmetry) and the two types of cubic  $3d$  functions were allowed different radial functions. The point charges were placed at a distance of 3.971 a.u. (the MgO nearest neighbor distance) from the  $Mn^{++}$  ion and calculations were done for charges of  $-1$  and  $-2$  at each charge site.

$Mn^{++}$ , with its half filled  $3d$  shell, is a rather special case. As a free ion its ground state is  $(3d)^5 {}^6S$  which has a spherical charge distribution. When all the radial functions of any given shell are the same and when

$$M_S = S = \frac{5}{2},$$

the Hartree-Fock ion wave function is a single determinant with all  $3d$  functions of one spin included. The determinant remains a  ${}^6S$  state if the five  $3d$  functions are put into their cubic form, i.e.,

$$\text{if } \left. \begin{array}{l} \psi_{3d}(m_\ell = +2) \\ \psi_{3d}(m_\ell = +1) \\ \psi_{3d}(m_\ell = 0) \\ \psi_{3d}(m_\ell = -1) \\ \psi_{3d}(m_\ell = -2) \end{array} \right\} \text{ are replaced by } \left\{ \begin{array}{l} \psi_{x^2-y^2} \text{ which equals } 2^{-\frac{1}{2}}[\psi_{3d}(m_\ell = +2) + \psi_{3d}(m_\ell = -2)] \\ \psi_{3z^2-r^2} \text{ which equals } \psi_{3d}(m_\ell = 0) \\ \psi_{xy} \text{ which equals } 2^{-\frac{1}{2}}[\psi_{3d}(m_\ell = +2) - \psi_{3d}(m_\ell = -2)] \\ \psi_{yz} \text{ which equals } 2^{-\frac{1}{2}}[\psi_{3d}(m_\ell = +1) - \psi_{3d}(m_\ell = -1)] \\ \psi_{zx} \text{ which equals } 2^{-\frac{1}{2}}[\psi_{3d}(m_\ell = +1) + \psi_{3d}(m_\ell = -1)]. \end{array} \right.$$

If the  $3d$  radial functions are constrained to be the same, the  $3d$  shell is spherical and will not interact with  $V_4(r)$ . As a result, a Hartree-Fock calculation for the ion in a cubic crystalline field would yield the free ion results. In the calculations to be described, the two types of cubic  $3d$  functions, the  $x^2-y^2$  and  $3z^2-r^2$

(henceforth denoted  $x^2-y^2$ ) on one hand and  $xy$ ,  $yz$ , and  $zx$  (henceforth denoted  $xy$ ) on the other, are allowed to have different radial functions. They will have different radial functions since they interact differently with a  $V_4(r)$ . Once the radial functions are not the same, the single determinant ceases to be a  ${}^6S$  state.

The point charge version of  $V_4(r)$  was chosen of necessity but I believe that it will serve very well for my purposes. A survey of the signs of experimental  $D_q$ 's tells us that it is the inner positive region of  $V_4(r)$

<sup>3</sup> The first truly self-consistent Hartree-Fock calculation for a nonclosed  $3d$  shell atom or ion was published by B. H. Worsley, Proc. Roy. Soc. (London) A247, 390 (1958). Since then, there has been work by D. F. Mayers [to be published in Proc. Roy. Soc. (London)] and the author.<sup>1,2</sup>

<sup>4</sup> W. H. Kleiner, J. Chem. Phys. 20, 1784 (1952).

<sup>5</sup> R. L. Mooney, Phys. Rev. 55, 557 (1939).

which is most important and this region will be quite well described by a point charge  $V_4(r)$  (perhaps with a charge between  $-1$  and  $-2$  for a doubly negative nearest neighbor ion). The purpose of this work is to explore the behavior of  $3d$  functions when solved for in cubic fields. The author is more interested in observing this behavior than in duplicating an experimental  $D_q$  thus an "accurate"  $V_4(r)$  is unnecessary. Comparison will be made between the results for different  $V_4(r)$ 's and not with experiment.

## II. CALCULATIONS

The calculations were done on the Whirlwind computer with the Roothaan procedure<sup>6</sup> as modified by Nesbet.<sup>7</sup> This is an analytic Hartree-Fock method and it produces one-electron radial wave functions ( $u_i(r)$ 's) which are linear combinations of normalized basis functions ( $\eta_j$ 's), i.e.,

$$u_i(r) = \sum_j C_{ij} \eta_j, \quad (2)$$

and in our case,

$$\eta_j \equiv N_j r^{n_j} e^{-z_j r}. \quad (3)$$

I have used the set of  $\eta_n$ 's which was used in my free  $Mn^{++}$   $6S$  Hartree-Fock calculation.<sup>1,2</sup> They are

	$j$	$n_j$	$z_j$	$N_j$
for the construction of $s$ functions	1	1	26.0651	266.14547
	2	2	22.7184	2840.6235
	3	2	11.4540	512.69885
	4	3	10.5661	1616.7403
	5	3	6.0612	231.15000
	6	3	3.8730	48.206424
for the construction of $p$ functions	7	2	16.0787	1197.0068
	8	2	9.5095	322.00567
	9	3	8.7370	831.20281
	10	3	4.9595	114.54373
	11	3	3.0743	21.480808
for the construction of $d$ functions	12	3	2.0235	4.9693541
	13	3	3.9754	52.816745
	14	3	7.4822	483.10479
	15	3	13.4624	3774.5700

An octahedral array of six point charges produces a spherical [ $V_0(r)$ ] and a cubic [ $V_4(r)$ ] potential.  $V_0(r)$  interacts with the  $s$ ,  $p$ , and  $d$  functions while  $V_4(r)$  interacts with only the  $d$  functions.  $V_0(r)$  is constant in the region inside of the point charges and falls off as  $1/r$  outside. The writer carried out Hartree-Fock calculations with  $V_0(r)$  included in the Hartree-Fock equations. It had almost no effect on the results as one would expect since only a small part of the  $Mn^{++}$  electronic charge is outside of the region where  $V_0(r)$  is constant.  $V_0(r)$  is neglected in the calculations which will be reported. Let us consider the  $V_4(r)$  contribution

<sup>6</sup> C. C. J. Roothaan, *Revs. Modern Phys.* **23**, 69 (1951).

<sup>7</sup> R. K. Nesbet, *Proc. Roy. Soc. (London)* **A230**, 312 (1955); *Quarterly Progress Reports* 15, 16, and 18, January, 1955, April, 1955, and October, 1955, *Solid-State and Molecular Theory Group*, Massachusetts Institute of Technology (unpublished), pp. 10, 38, 41, and 4, respectively.

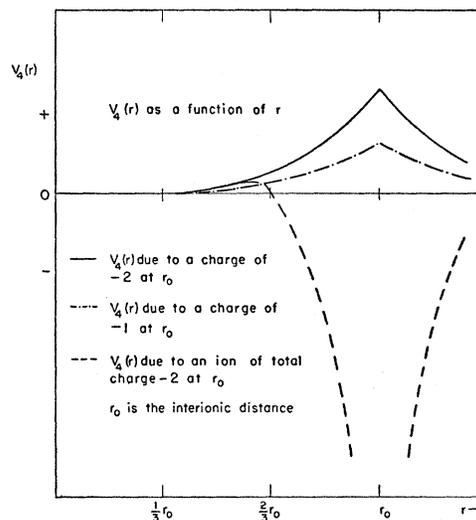


FIG. 1.  $V_4(r)$  as a function of  $r$ .

and define

$$V^4(i, j) \equiv \int_0^\infty u_i(r) u_j(r) V_4(r) dr, \quad (4)$$

where

$$V_4(r) \equiv \begin{cases} r^4/r_0^5 & \text{for } r < r_0, \\ r_0^4/r^5 & \text{for } r > r_0, \end{cases} \quad (5)$$

where  $r_0$  is the nearest neighbor distance (3.971 a.u. in these calculations). The crystalline field splitting is normally defined as  $10D_q$  and if the two types of  $3d$  functions have the same radial dependence,  $10D_q$ , for the point charge  $V_4(r)$ , is

$$10D_q = +5\delta\{[7 + (70)^{1/2}]/21\} V^4(3d, 3d). \quad (6)$$

$\delta$  is the magnitude of a single point charge or 1 and 2 in these calculations. The "crystalline field splitting" must be redefined for the case of two different  $3d$  radial functions. This requires an investigation of the contributions  $V_4(r)$  makes to the  $3d$  one-electron energies. The contribution to the  $xy$  one-electron energy is

$$-2\delta\{[7 + (70)^{1/2}]/21\} V^4(xy, xy), \quad (7)$$

and for the  $x^2 - y^2$  function it is

$$+3\delta\{[7 + (70)^{1/2}]/21\} V^4(x^2 - y^2, x^2 - y^2). \quad (8)$$

It should be noted that the magnitude of each contribution is proportional to the degeneracy of the other type of function. The  $10D_q$  is normally defined as the change in the crystalline field contribution to the ion's total energy when an  $xy$  function is replaced by an  $x^2 - y^2$  function and when each type of one-electron function has the same radial dependence for both the initial and the final ionic state. In other words,  $10D_q$  is simply Eq. (8) minus Eq. (7). This yields Eq. (6) if  $V^4(xy, xy)$  equals  $V^4(x^2 - y^2, x^2 - y^2)$  and if the integrals

are not equal, one obtains

$$10D_q = \mathfrak{z}\{[7 + (70)^{\frac{1}{2}}]/21\}[2V^4(xy, xy) + 3V^4(x^2 - y^2, x^2 - y^2)]. \quad (9)$$

This expression will be used below.

The Hartree-Fock equations for the  $3d$  functions appear in Appendix I. They are rather different than the free  $Mn^{++}$   $3d$  Hartree-Fock equations despite the fact that they become the free ion equations when  $V_4(r)$  is removed and  $u_{xy}(r)$  equals  $u_{x^2-y^2}(r)$ . Except for the contributions from two rather than one type of  $3d$  function, the Hartree-Fock equations for the other occupied shells are identical with the free ion ones and will not be reported by the author.

### III. RESULTS

The combining coefficients ( $C_{ij}$ ), which define the final  $u_i(r)$ 's in terms of the basis set, are to be found in

TABLE I. Combining coefficients ( $C_{ij}$ ).

	Free $Mn^{++}$	$Mn^{++}$ in cubic field with $\mathfrak{z}=1$	$Mn^{++}$ in cubic field with $\mathfrak{z}=2$
<i>i=1s</i>			
1	+0.92029428	+0.92029500	+0.92029333
2	+0.09863379	+0.09863225	+0.09863773
3	-0.00313726	-0.00313536	-0.00314522
4	+0.00225118	+0.00224963	+0.00225925
5	-0.00055350	-0.00055296	-0.00055769
6	+0.00011878	+0.00011861	+0.00012049
<i>i=2s</i>			
1	-0.27738741	-0.27738803	-0.27738782
2	-0.16713964	-0.16714428	-0.16714516
3	+0.76012694	+0.76014226	+0.76014292
4	+0.38685587	+0.38684234	+0.38684394
5	+0.02478087	+0.02478395	+0.02478226
6	-0.00143917	-0.00144142	-0.00144357
<i>i=3s</i>			
1	+0.10216923	+0.10217357	+0.10218396
2	+0.05842931	+0.05842772	+0.05841713
3	-0.27459472	-0.27459093	-0.27455994
4	-0.32927989	-0.32933381	-0.32948726
5	+0.39384716	+0.39396989	+0.39426818
6	+0.79950612	+0.79942190	+0.79922133
<i>i=2p</i>			
7	+0.15937739	+0.15938378	+0.15937851
8	+0.84954106	+0.84952920	+0.84954172
9	+0.00512492	+0.00513839	+0.00512818
10	+0.01961790	+0.01960454	+0.01960767
11	-0.00422519	-0.00422027	-0.00422369
<i>i=3p</i>			
7	-0.04780407	-0.04781460	-0.04783557
8	-0.33758535	-0.33758470	-0.33758282
9	-0.01405616	-0.01409630	-0.01418821
10	+0.63249462	+0.63265198	+0.63298088
11	+0.49397930	+0.49384790	+0.49357649
<i>i=3d</i>			
		<i>i=x<sup>2</sup>-y<sup>2</sup></i>	
12	+0.44792419	+0.42604735	+0.40519961
13	+0.55374026	+0.57452833	+0.59402656
14	+0.13477286	+0.13236102	+0.13015887
15	+0.00633154	+0.00737900	+0.00834895
		<i>i=xy</i>	
12		+0.46290931	+0.47822797
13		+0.53928142	+0.52433174
14		+0.13652402	+0.13837197
15		+0.00559107	+0.00481742

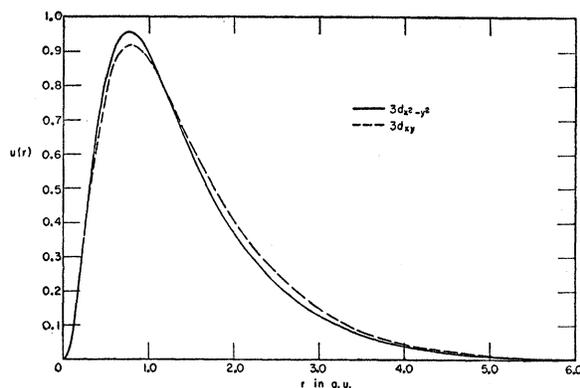


FIG. 2.  $3d$  radial wave functions as a function of  $r$  for the Hartree-Fock calculation for  $Mn^{++}$  in the  $-2$  charge  $V_4(r)$  potential.

Table I. The  $C_{ij}$ 's for the author's free  $Mn^{++}$   ${}^6S$  calculation appear there along with those for calculations with  $\mathfrak{z}$  equal to 1 and 2. The  $u_{x^2-y^2}(r)$  and  $u_{xy}(r)$  for the  $\mathfrak{z}=2$  calculation are graphed in Fig. 2. Table II lists a number of one- and two-electron integrals. The  $K(i)$ 's are the one-electron kinetic plus nuclear potential energy integrals.  $V^4(3d, 3d)$  contributions are not included in the  $K(3d)$ 's. All the two-electron  $F^k(i, j)$  and  $G^k(i, j)$  integrals that contribute to the ion's total energy are included in the table. Inspection of the table shows that the  $F^k(xy, xy)$ 's and  $F^k(x^2 - y^2, x^2 - y^2)$  differ with each other by about ten percent and the  $V^4(3d, 3d)$ 's show a twenty percent difference for the  $\mathfrak{z}=2$  calculations. The differences are approximately half as great for the  $\mathfrak{z}=1$  calculation.

The total energies of the ions will be found in Table III. The energies have been tabulated both with and without the contributions from the cubic fields. We should note that the  $V^4(3d, 3d)$  contributions to the total energies would equal zero if the two types of  $3d$  radial functions were constrained to be the same. Lack of common radial functions leads to total energy contributions of  $\sim -370$   $cm^{-1}$  (0.0034 ry) for the  $\mathfrak{z}=1$  calculation and  $\sim -2180$   $cm^{-1}$  (0.0199 ry) for  $\mathfrak{z}=2$ . Another feature of interest is the fact that the free ion total energy is stable for rather substantial variations of the  $3d$  electrons.

If we use Eq. (9) and calculate  $10D_q$  for the  $\mathfrak{z}=1$  solution, we would obtain

$$10D_q = 4275 \text{ cm}^{-1}, \quad (10)$$

and for the  $\mathfrak{z}=2$  solution,

$$10D_q = 8412 \text{ cm}^{-1} \text{ for a } \mathfrak{z}=2 \text{ field,} \\ \text{or } 4206 \text{ cm}^{-1} \text{ for a } \mathfrak{z}=1 \text{ field.} \quad (11)$$

Note the rather good agreement when  $10D_q$  is computed for the same field.

TABLE II. One- and two-electron integrals all integrals are in Hartree units (1 a.u. = 2 ry).

One-electron kinetic +nuclear potential energy integrals <sup>a</sup>	Free Mn <sup>++</sup> <sup>b</sup>	Mn <sup>++</sup> in cubic field with $\delta=1$	Mn <sup>++</sup> in cubic field with $\delta=2$
$K(1s) =$	-312.3568	-312.3568	-312.3568
$K(2s) =$	-76.34235	-76.34245	-76.34249
$K(3s) =$	-29.24340	-29.24393	-29.24516
$K(2p) =$	-75.66955	-75.66961	-75.66963
$K(3p) =$	-27.44747	-27.44840	-27.45030
$K(x^2-y^2) =$	-22.95467	-23.18053	-23.38148
$K(xy) =$	-22.95467	-22.79803	-22.64472
Cubic potential integrals			
$V^4(x^2-y^2, x^2-y^2) =$	...	+0.005093	+0.004783
$V^4(xy, xy) =$	...	+0.005669	+0.005918
Two-electron integrals			
$F^0(1s, 1s) =$	+15.27457	+15.27458	+15.27457
$F^0(1s, 2s) =$	+4.527865	+4.527879	+4.527881
$F^0(1s, 3s) =$	+1.525485	+1.525534	+1.525647
$F^0(2s, 2s) =$	+3.222584	+3.222595	+3.222598
$F^0(2s, 3s) =$	+1.370124	+1.370162	+1.370247
$F^0(3s, 3s) =$	+1.045595	+1.045625	+1.045692
$G^0(1s, 2s) =$	+0.4120717	+0.4120749	+0.4120748
$G^0(1s, 3s) =$	+0.0514755	+0.0514795	+0.0514885
$G^0(2s, 3s) =$	+0.0879206	+0.0879270	+0.0879410
$F^2(2p, 2p) =$	+1.740557	+1.740561	+1.740565
$F^0(2p, 2p) =$	+3.689427	+3.689435	+3.689441
$F^2(2p, 3p) =$	+0.2586813	+0.2587060	+0.2587584
$F^0(2p, 3p) =$	+1.345266	+1.345330	+1.345628
$F^2(3p, 3p) =$	+0.4983987	+0.4984278	+0.4984874
$F^0(3p, 3p) =$	+0.9909815	+0.9910341	+0.9911421
$F^0(1s, 2p) =$	+5.064964	+5.064976	+5.064979
$F^0(2s, 2p) =$	+3.406107	+3.406117	+3.406121
$F^0(3s, 2p) =$	+1.389760	+1.389799	+1.389888
$F^0(1s, 3p) =$	+1.479725	+1.479805	+1.479971
$F^0(2s, 3p) =$	+1.320804	+1.320866	+1.320993
$F^0(3s, 3p) =$	+1.017079	+1.017121	+1.017210
$G^2(2p, 3p) =$	+0.1029035	+0.1029145	+0.1029390
$G^0(2p, 3p) =$	+0.0984245	+0.0984344	+0.0984566
$G^1(1s, 2p) =$	+0.8413449	+0.8413503	+0.8413494
$G^1(2s, 2p) =$	+1.969162	+1.969166	+1.969170
$G^1(3s, 2p) =$	+0.1092325	+0.1092400	+0.1092585
$G^1(1s, 3p) =$	+0.0922210	+0.0922210	+0.0922557
$G^1(2s, 3p) =$	+0.0759137	+0.0759221	+0.0759400
$G^1(3s, 3p) =$	+0.6771183	+0.6771471	+0.6772008
$F^0(1s, x^2-y^2) =$	+1.182755	+1.197706	+1.211790
$F^0(1s, xy) =$	...	+1.172445	+1.1618297
$F^0(2s, x^2-y^2) =$	+1.163578	+1.177993	+1.191563
$F^0(2s, xy) =$	...	+1.153633	+1.143389
$F^0(3s, x^2-y^2) =$	+0.9267982	+0.9351254	+0.9429348
$F^0(3s, xy) =$	...	+0.9210356	+0.9150887
$F^2(2p, x^2-y^2) =$	+0.2091691	+0.2141237	+0.2188225
$F^0(2p, x^2-y^2) =$	+1.168254	+1.182797	+1.196490
$F^2(2p, xy) =$	...	+0.2057758	+0.2022991
$F^0(2p, xy) =$	...	+1.158221	+1.147888
$F^2(3p, x^2-y^2) =$	+0.4299220	+0.4352828	+0.4402856
$F^0(3p, x^2-y^2) =$	+0.9047634	+0.9126404	+0.9200358
$F^2(3p, xy) =$	...	+0.4261950	+0.4223340
$F^0(3p, xy) =$	...	+0.8993297	+0.8937290
$G^2(1s, x^2-y^2) =$	+0.0015268	+0.0015785	+0.0016279
$G^2(1s, xy) =$	...	+0.0014917	+0.0014559
$G^2(2s, x^2-y^2) =$	+0.1357821	+0.1393893	+0.1428270
$G^2(2s, xy) =$	...	+0.1333253	+0.1308172
$G^2(3s, x^2-y^2) =$	+0.4072187	+0.4135672	+0.4194496
$G^2(3s, xy) =$	...	+0.4027675	+0.3981314
$G^2(2p, x^2-y^2) =$	+0.0838768	+0.0861199	+0.0882477
$G^1(2p, x^2-y^2) =$	+0.1478107	+0.1517688	+0.1555409
$G^2(2p, xy) =$	...	+0.0823530	+0.0807976
$G^1(2p, xy) =$	...	+0.1451140	+0.1423610
$G^2(3p, x^2-y^2) =$	+0.3241195	+0.3288204	+0.3331787
$G^1(3p, x^2-y^2) =$	+0.5364174	+0.5433762	+0.5497815
$G^2(3p, xy) =$	...	+0.3208290	+0.3174036
$G^1(3p, xy) =$	...	+0.5315151	+0.5263860
$F^4(x^2-y^2, x^2-y^2) =$	+0.2421857	+0.2476004	+0.2528356
$F^2(x^2-y^2, x^2-y^2) =$	+0.3887046	+0.3967594	+0.4045186
$F^0(x^2-y^2, x^2-y^2) =$	+0.8365658	+0.8499700	+0.8627338
$F^4(x^2-y^2, xy) =$	...	+0.2429033	+0.2432059
$F^2(x^2-y^2, xy) =$	...	+0.3897936	+0.3903004
$F^0(x^2-y^2, xy) =$	...	+0.8385069	+0.8396903
$F^4(xy, xy) =$	...	+0.2385296	+0.2348411
$F^2(xy, xy) =$	...	+0.3832489	+0.3777284
$F^0(xy, xy) =$	...	+0.8274010	+0.8180426
$G^4(x^2-y^2, xy) =$	...	+0.2428799	+0.2431146
$G^2(x^2-y^2, xy) =$	...	+0.3897187	+0.3900068
$G^0(x^2-y^2, xy) =$	...	+0.8381233	+0.8381804

<sup>a</sup>  $V^4(3d, 3d)$  is not included in the  $K(3d)$  integrals.

<sup>b</sup> The integrals involving the free Mn<sup>++</sup>  $3d$  function will be listed as  $x^2-y^2$ .

If one inserts individual  $V^4(3d, 3d)$ 's into Eq. (6) one can produce other estimates of  $10D_q$ . If we do this for

TABLE III. Ion total energies.

Free Mn <sup>++</sup>	-2298.2098 rydbergs
$\delta=1$ Mn <sup>++</sup> with $\delta=1$ cubic field	-2298.2127
$\delta=1$ Mn <sup>++</sup> with no cubic field	-2298.2093
$\delta=2$ Mn <sup>++</sup> with $\delta=2$ cubic field	-2298.2203
$\delta=2$ Mn <sup>++</sup> with no cubic field	-2298.2004

the  $\delta=2$  solutions we obtain

$$10D_q = 2 \times 5 \{ [7 + (70)^{1/2}] / 21 \} V^4(x^2-y^2, x^2-y^2) = \sim 7680 \text{ cm}^{-1}, \quad (12)$$

and

$$10D_q = 2 \times 5 \{ [7 + (70)^{1/2}] / 21 \} V^4(xy, xy) = \sim 9500 \text{ cm}^{-1}. \quad (13)$$

#### IV. CONCLUSIONS

If one wishes to calculate a  $10D_q$  to a numerical accuracy of 100 to 400 cm<sup>-1</sup>, one should obtain one-electron wave functions by doing a calculation for the ion in a crystalline field with solutions for two different  $u_{3d}(r)$ 's. A single  $u_{3d}(r)$  could be used if one is attempting a less accurate crystalline field calculation.

There is no obvious best way for obtaining the single  $u_{3d}(r)$ . A Hartree-Fock calculation for an ion in a crystalline field will not always be a better source than a free ion calculation. For example, let us consider an ion with a single  $3d$  electron. We wish a  $u_{3d}(r)$  which can reasonably represent either  $u_{xy}(r)$  or  $u_{x^2-y^2}(r)$  but a Hartree-Fock calculation for the ion in a cubic field, with an  $xy$  electron present, would lead to a  $u_{3d}(r)$  which is a quite unreasonable  $u_{x^2-y^2}(r)$ . A large  $V^4(3d, 3d)$  and in turn a large  $D_q$  would occur. A Hartree-Fock calculation with an  $x^2-y^2$  electron present, would lead to a much smaller  $D_q$ . Equations (12) and (13) indicate the sort of thing which would happen (although the Mn<sup>++</sup> situation is really different). Perhaps the most reasonable source for a single  $u_{3d}(r)$  would be a calculation where Hartree-Fock equations have been derived for two states of the ion (one state with one more  $xy$  and one less  $x^2-y^2$  function than the other) and where the averages of the Hartree-Fock equations for the two states are solved.

It has been the author's experience<sup>1,2,8</sup> that free ion Hartree-Fock calculations for different states of the same ion lead to variations of the one-electron wave functions which are energetically significant. In other words, the assumption of a common set of radial functions for different states of the ion is a poor one and perhaps we must abandon thinking of the parameters [ $F^k(i, j)$ 's, etc.] as simple one- and two-electron integrals. If we wish accurate predictions of the optical absorption spectra, we will have to investigate the added contributions to the parameters. This in-

<sup>8</sup> R. E. Watson, Quarterly Progress Report No. 27, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, January, 1958 (unpublished), p. 10.

vestigation will be difficult. One possible starting point would be a set of variational calculations for individual ion states and then a comparison of the differences in their total energies with the experimental spectra. The author's results show that it will be imperative to handle the two types of  $3d$  electrons separately. We have seen shifts of 370 and 2180  $cm^{-1}$  in the ion's total energy due to letting  $u_{xy}(r)$  and

$u_{x^2-y^2}(r)$  differ. These are appreciable energy shifts and their source should not be neglected.

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#### APPENDIX I. THE $3d$ HARTREE-FOCK EQUATIONS

The  $3d$  Hartree-Fock equations are

$$\begin{aligned} \epsilon_{x^2-y^2} u_{x^2-y^2}(r) = & \left( -\frac{d^2}{dr^2} - \frac{2Z}{r} + \frac{\ell(\ell+1)}{r^2} \right) u_{x^2-y^2}(r) + [2Y^0(1s,1s) + 2Y^0(2s,2s) + 2Y^0(3s,3s) + 6Y^0(2p,2p) \\ & + 6Y^0(3p,3p) + 2Y^0(x^2-y^2, x^2-y^2) + 3Y^0(xy,xy) + 1.21428571Y^4(x^2-y^2, x^2-y^2) \\ & - 1.21428571Y^4(xy,xy)] [u_{x^2-y^2}(r)]/r - (1/r) [Y^2(x^2-y^2, 1s)u_{1s}(r) + Y^2(x^2-y^2, 2s)u_{2s}(r) \\ & + Y^2(x^2-y^2, 3s)u_{3s}(r) + 1.2Y^1(x^2-y^2, 2p)u_{2p}(r) + 1.8Y^3(x^2-y^2, 2p)u_{2p}(r) \\ & + 1.2Y^1(x^2-y^2, 3p)u_{3p}(r) + 1.8Y^3(x^2-y^2, 3p)u_{3p}(r) + 1.0Y^0(x^2-y^2, x^2-y^2)u_{x^2-y^2}(r) \\ & + 0.81632653Y^2(x^2-y^2, x^2-y^2)u_{x^2-y^2}(r) + 1.04081632Y^4(x^2-y^2, x^2-y^2)u_{x^2-y^2}(r) \\ & + 0.61224490Y^2(xy, x^2-y^2)u_{xy}(r) + 1.53061224Y^4(xy, x^2-y^2)u_{xy}(r)] \\ & + \{3[7 + (70)^{1/2}]/21\} \partial V_4(r) u_{x^2-y^2}(r), \end{aligned}$$

and

$$\begin{aligned} \epsilon_{xy} u_{xy}(r) = & \left( -\frac{d^2}{dr^2} - \frac{2Z}{r} + \frac{\ell(\ell+1)}{r^2} \right) u_{xy}(r) + [2Y^0(1s,1s) + 2Y^0(2s,2s) + 2Y^0(3s,3s) + 6Y^0(2p,2p) + 6Y^0(3p,3p) \\ & + 2Y^0(x^2-y^2, x^2-y^2) + 3Y^0(xy,xy) - 0.80952381Y^4(x^2-y^2, x^2-y^2) + 0.80952381Y^4(xy,xy)] u_{xy}(r)/r \\ & - (1/r) [Y^2(xy,1s)u_{1s}(r) + Y^2(xy,2s)u_{2s}(r) + Y^2(xy,3s)u_{3s}(r) + 1.2Y^1(xy,2p)u_{2p}(r) \\ & + 1.8Y^3(xy,2p)u_{2p}(r) + 1.2Y^1(xy,3p)u_{3p}(r) + 1.8Y^3(xy,3p)u_{3p}(r) + 0.40816326Y^2(xy, x^2-y^2)u_{x^2-y^2}(r) \\ & + 1.02040816Y^4(xy, x^2-y^2)u_{x^2-y^2}(r) + Y^0(xy,xy)u_{xy}(r) + 1.02040816Y^2(xy,xy)u_{xy}(r) \\ & + 1.55102041Y^4(xy,xy)u_{xy}(r)] - \{2[7 + (70)^{1/2}]/21\} \partial V_4(r) u_{xy}(r), \end{aligned}$$

where  $Z$  is the ion nuclear charge and

$$Y^k(i,j) = 2 \int_r^r u_i(r') u_j(r') (r'/r)^k dr' + 2 \int_r^\infty u_i(r') u_j(r') (r'/r)^{k+1} dr'.$$

Note the  $Y^4(x^2-y^2, x^2-y^2)$  and  $Y^4(xy,xy)$  terms in the second brackets. These terms do not appear in the free ion equations. Their effect is to repel like  $d$  electrons and attract unlike  $3d$  electrons thus resisting the effect of the  $V_4(r)$  terms.