The matrix elements of S_z can be calculated by using the above wave functions; and using formula (10) we obtain the theoretical absorption spectrum of the oxygen molecule as shown in Fig. 3.

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Antishielding and Contracted Wave Functions

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The antishielding factors, γ_∞, of several contracted negative ions are calculated and compared to the apparent experimental values. Although the use of contracted wave functions results in considerably smaller γ_∞'s, the agreement is still not encouraging for the negative ions. Interrelations are found among the wave functions contracted by different means. Also, γ_∞ of several closed-shell positive ions and two ^6S state ions (Mn^{+2} and Fe^{+3}) are calculated so that information from measured quadrupole coupling constants can be obtained. These positive-ion results with other published values should enable γ_∞ of all closed-shell ions to be estimated. The results are used to determine the nuclear quadrupole moment of Fe^{57m} from the published value of the quadrupole coupling constant in Fe_2O_3. This result is discussed.

I. INTRODUCTION

IN calculations using atomic wave functions it is known that large differences can occur in the result if Hartree (H.) rather than Hartree-Fock (H.F.) functions are used. For example, calculations of the binding energies of alkali halide crystals[1] give better agreement with experiment when H.F. rather than more diffuse H. wave functions are used. Recently, various authors have calculated contracted wave functions.[2–6] These functions attempt to take into account the actual fields in which the ion is situated with the result that even better binding energies are obtained.

In this paper contracted wave functions are used to calculate atomic polarizabilities and the Sternheimer antishielding factors[7] for several ions. Comparison is made with the results obtained from the free ion H. and H.F. functions and with experimental results in order to obtain a more complete understanding of the applicability and interrelationship among the wave functions. Antishielding factors are also calculated for several closed shell positive ions and for Fe^{+3} and Mn^{+2}, which are in a ^6S state. These values are required to interpret quadrupole coupling data.

II. CONTRACTION OF WAVE FUNCTIONS

To obtain the wave functions used in this paper, several methods were needed and will be briefly described.

1. O^{-2}: Watson[6] has calculated analytic H.F. wave functions for O^{-2} ions that are in a sphere of charge with the radius of the sphere equal to the ionic radius. The wave functions were calculated for a charge of $+2$ and $+1$, on the stabilizing sphere. These wave functions are called $O^{-2}(+2w)$ and $O^{-2}(+1w)$, respectively. The $2p$ wave functions have five parameters and the $1s$ and $2s$ wave functions have seven parameters.

2. O^{-2}: Yamashita and Kajima[3] have calculated the wave functions for O^{-2} in $Mg^{+2}O^{-2}$ by assuming an analytic form for the $2p$ wave function with three parameters. The parameters are varied to minimize the energy of the entire crystal rather than the free ion alone. For the $1s$ and $2s$ wave function they took the H.F. O^{-1} wave function and used the H.F. wave function of Mg^{+2}. The calculation was done for the observed crystal spacing. The wave function is called $O^{-2}(MgO)$.

3. F^{-1}: Yamashita[4] has calculated the F^{-1} wave function in a manner similar to the O^{-2} calculation. The $2p$ wave function of F^{-1} has three parameters and

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[1] See P. O. Lowdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Sec. 7 for a convenient summary.

[2] G. C. Benson and G. Wyllie, Proc. Soc. (London) **A64**, 276 (1951).

[3] J. Yamashita and M. Kajima, J. Phys. Soc. (Japan) **7**, 261 (1952).

[4] J. Yamashita, J. Phys. Soc. (Japan) **7**, 284 (1952).

[5] R. Gaspar and P. Csavinszky, Acta. Sci. Hung. **5**, 65 (1955); see also **6**, 125 (1956).

[6] R. E. Watson, Phys. Rev. **111**, 1108 (1958).

[7] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954); R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956); R. M. Sternheimer, Phys. Rev. **84**, 244 (1951).

TABLE I. Polarizabilities, antishielding factors, and expectation values of the outer *p*-wave functions for contracted negative ions.

	O^{-2}(MgO)[a]	$O^{-2}(+2w)$	$O^{-2}(+1w)$	F^{-1}(H.)	F^{-1}(H.F.)	F^{-1}(free)	F^{-1}(3.7)	Cl^{-1}(H.)	Cl^{-1}(H.F.)	$Cl^{-1}(x)$
$\alpha_D(p \rightarrow d)$, A^3	2.914	2.741	3.668	3.432	1.237	1.313	1.113	12.23	5.026	2.982
$\alpha_Q(p \rightarrow f)$, A^5	3.495	4.178	6.985	10.52	1.493	1.277	0.9768	43.42	7.780	3.811
$\alpha_Q(p \rightarrow p)$, A^5	2.743	3.560	6.242	11.24	1.384	1.105	0.8256	37.35	5.322	2.728
$\gamma_\infty(p \rightarrow p)$	−28.22	−25.30	−33.90	−66.86	−23.22	−25.71	−21.11	−158.5	−50.07	−27.04
$\langle r^{-3}\rangle$[b]	2.537	3.320	3.169	5.676	6.404	4.649	4.728	5.452	5.740	
$\langle r^{-2}\rangle$	1.157	1.334	1.269	1.885	2.082	1.776	1.806	0.9699	1.042	
$\langle r^{-1}\rangle$	0.8729	0.9224	0.8900	1.087	1.162	1.096	1.106	0.6218	0.6785	
$\langle r^{1}\rangle$	1.647	1.589	1.675	1.446	1.257	1.306	1.271	2.369	2.036	1.798
$\langle r^{2}\rangle$	3.673	3.468	3.906	3.194	2.211	2.357	2.200	7.388	5.151	4.022
$\langle r^{3}\rangle$	10.41	9.836	12.04	10.39	5.248	5.597	4.979	30.05	15.98	11.02
$\langle r^{4}\rangle$	35.54	34.98	47.31	46.94	16.13	16.53	13.98	157.5	60.23	36.70
$\langle r^{5}\rangle$	140.5	152.4	229.2	277.1	61.68	57.93	46.59	1037	272.6	149.1

[a] For references to the original papers describing the wave function calculations see Sec. I or II. For references to F^{-1}(H.), Cl^{-1}(H.), and Cl^{-1}(H.F.) see R. Knox, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957) Vol. 4, p. 413. For F^{-1}(H.F.) see C. Froese, Proc. Cambridge Phil. Soc. **3**, 206 (1957).

[b] The values for $\langle r^n\rangle$ are in atomic units.

for the 1*s* and 2*s* wave functions he used the H. wave function for F^{-1}. The H.F. wave function for Li^{+} was used. The calculation was done for several lattice spacings and besides the $Li^{+1}-F^{-1}$ interaction, the $F^{-1}-F^{-1}$ interaction was taken into account. The resulting wave function is labeled F^{-1}(3.7). Agreement of cohesive energy and lattice constant with experiment is good. Further, the calculation for free F^{-1}, F^{-1}(free), was done also.

4. Cl^{-1}: No previously contracted wave functions for Cl^{-1} are known. The diamagnetic susceptibility from the H.F. wave function for the free Cl^{-1} ion[8] is -30.4×10^{-6} while the value measured[9] in solids is -25×10^{-6}. The 3*p* wave function in Cl^{-1} contributes 80% of the calculated value. Thus, in lieu of a rigorous calculation of the contracted wave function of Cl^{-1}, the 3*p* wave function was contracted by a linear scale factor so that the experimental susceptibility would be obtained.[10] The 3*p* wave function should be kept orthogonal to the 2*p* wave function; this requirement enters explicitly when γ_∞ is calculated. Later, it is shown that the inner parts of the wave function are hardly affected by the contraction. Thus, it is considered a reasonable approximation to contract only the outer parts of the Cl^{-1} ion (i.e., the moments $\langle r^{+2}\rangle$ to $\langle r^{+5}\rangle$) and leave the inner part the same so that the 3*p* is still orthogonal to the 2*p*. This wave function is called $Cl^{-1}(x)$.

The other wave functions that will be used for comparison are those calculated for the free ions by the H. and H.F. method.

III. POLARIZABILITY AND ANTISHIELDING FACTOR

The polarizabilities are calculated by a variation of parameters method.[11] The form of the radial part of the excited state wave function used is $\beta r H_1(r)u_0'$, where $H_1(r)$ is the radial part of the perturbation, u_0' is the radial part of the unperturbed wave function, and β is a coefficient determined by the minimization of energy procedure. This form of wave function has been previously discussed and shown to a very good choice.[11,12] For γ_∞ of F^{-1} and O^{-2}, a form $(\alpha+\beta r)H_1(r)u_0'$ was used. For the other wave functions that contain more than one shell of *p* electrons care must be taken because of orthogonalization requirements.[13]

As first shown by Foley, Sternheimer, and Tycko,[7] the antishielding factor is needed in the interpretation of nuclear quadrupole coupling data, eQq/h, in ionic substances. Since then γ_∞ has been calculated for various ions.[7,11–15] In general, good agreement is obtained between theoretical calculations and experimental results for γ_∞ of positive ions. For example, Bersohn[16] has shown this to be true for Na^{+1} in $NaNO_3$, and $NaClO_3$ although only fair agreement is obtained for Cu^{+1} in Cu_2O and for Al^{+3} in Al_2O_3 and poor agreement for Na^{+1} in $NaBrO_3$. In alkali halide gases agreement is good for the alkali ions.[12] Experimental evidence from the ultrasonic work[17,18] on Na^{+1} and the temperature dependence of eQq/h for Al^{+3} in $C(NH_2)_3Al(SO_4)_2\cdot6H_2O$[19] together with the comparison of the temperature dependence of eQq/h of Al^{+3} and Ga^{+3} in isomorphous compounds[20] indicates agreement exists between theory and experiment. The evidence from relaxation time measurements is less clear. Valiev[21]

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[8] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936).

[9] G. W. Brindley and F. E. Hoare, Proc. Roy. Soc. (London) **A152**, 342 (1935).

[10] The scale factor was 1.132. Of course, the wave function must be kept normalized.

[11] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

[12] G. Burns, Phys. Rev. **115**, 357 (1959).

[13] E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).

[14] G. Burns, J. Chem. Phys. **31**, 1253 (1959).

[15] R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959).

[16] R. Bersohn, J. Chem. Phys. **29**, 326 (1958). See also R. A. Bernheim and H. S. Gutowsky, J. Chem. Phys. **32**, 1072 (1960).

[17] W. G. Proctor and W. A. Robinson, Phys. Rev. **104**, 1344 (1956).

[18] E. F. Taylor and N. Bloembergen, Phys. Rev. **113**, 431 (1959).

[19] G. Burns, Bull. Am. Phys. Soc. **3**, 371 (1958). A full account of the results on $C(NH_2)_3Al(SO_4)_2\cdot6H_2O$(GASH) and its isomorphous compounds is in preparation.

[20] G. Burns, Bull. Am. Phys. Soc. **5**, 253 (1960).

[21] K. A. Valiev, J. Exptl. Theoret. Phys. (U.S.S.R.) **37**, 109 (1959) [translation: Soviet Phys.-JETP **37**, 77 (1960)].

TABLE II. Antishielding factors for positive ions.

	Cu^{+1}(H.)[a]	Ga^{+3}(H.F.)	Kr(H.F.)	Ag^{+1}(H.F.)	Ag^{+1}(H.)	In^{+3}(H.)	Mn^{+2}(H.F.)	Fe^{+3}(H.F.)
$2p \to p$	−0.58	−0.56	−0.43	−0.30	−0.32	−0.32	−0.50	−0.68
$3p \to p$	−13.01	−4.08	−2.40	−0.97	−1.06	−1.06	−5.00	−5.00
$3d \to d$	−16.7	−3.09	−1.48	−0.51	−0.55	−0.55	−2.39	−1.53
$4p \to p$			−38.75	−10.91	−11.87	−7.41		
$4d \to d$				−11.32	−22.86	−7.89		
Angular contribution	+1.19	+0.79	+2.1	+1.9	+1.9	+1.9	+1.08	+1.04
Total	−29.10	−6.94	−40.96	−22.11	−34.76	−15.33	−6.81	−6.17

[a] The references for the wave functions can be found in the article by R. Knox quoted in Fig. 1. For Mn^{+2} and Fe^{+3} see reference 35. For Kr(H.F.) and Ag^+ see B. H. Worsley, Roy. Soc. Proc. (London) **A247**, 390 (1958). For Ga^{+3}(H.F.) see W. W. Piper (to be published). It is a pleasure to thank Dr. Piper for sending his wave functions prior to publication.

obtains reasonable results for $(1-\gamma_\infty)^2$ from considerations of the line width of Al^{+3} and Ga^{+3} in solutions. In alkali halide crystals Wikner *et al.*[22] show that the ionic model is important and is in agreement with experiment in some crystals but for others, covalent considerations predict shorter spin lattice relaxation times so one can not check the predictions of the ionic model.

For negative ions there is little agreement between theory and experiment. The halide ions in alkali gases have a great deal of scatter in their antishielding factors[23] and simple considerations of covalent effects[13] or induced moments in the alkali[12] ion do not help. The results form ultrasonic experiments,[18,24,25] mixed crystal experiments,[26–28] and dislocation studies[29] for Cl^{-1}, Br^{-1}, and I^{-1} indicate there is no agreement between theory and experiment. However, the experimental results do seem to center about $\gamma_\infty = 10$, 35, and 45, respectively. While the theoretical calculations are about four times larger. The higher symmetry and larger internuclear distances in the solids result in perturbations of these easily deformable negative ions, that are smaller than in the alkali halide gases. Thus, it seems reasonable to investigate the effect of contraction on these negative ions to see if agreement is possible.

IV. RESULTS AND CONCLUSIONS

Table I contains the results for the polarizabilities and γ_∞ calculations and the various moments of the distributions for the negative ions where $\langle r^n \rangle$ has the usual definition,

$$\langle r^n \rangle = \int_0^\infty (u_0^2) r^n dr.$$

Not all of the possible contributions to the polarizabilities are listed. The dipole polarizability, α_D, also has a contribution from $s \to p$ and $p \to s$ but these tend to cancel one another,[30–32] are small compared to the contribution listed, and here, the interest is on the effects of contraction. The total quadrupole polarizability also contains an $s \to d$ contribution, but it is much smaller than the listed contributions.[14,33] The antishielding factor, γ_∞, contains, besides the $p \to p$ contribution, the $s \to d$ and $p \to f$ and $p \to p$ from the inner shells, i.e., $2p$ shell for Cl^{-1}. However, these are small and have opposite signs so they need not be considered for these negative ions since errors in the $p \to p$ contribution listed, due to lack of knowledge of the proper wave functions, far overshadow these small contributions.

Certain conclusions are obvious from Table I.

1. Contraction can have large effects on the polarizabilities and antishielding factors. The dipole polarizabilities are in better agreement with experiment.[34]

2. Contraction of a wave function has little effect on the electron distribution at small r.

3. The inner parts of the wave functions are the most difficult to obtain accurately. Thus, the moments sampling the outer parts of $O^{-2}(+2w)$ and O^{-2}(MgO) and of F^{-1}(free) and F^{-1}(H.F.) are very similar but the $\langle r^{-3} \rangle$'s differ.

4. The results from the somewhat arbitrary O^{-2} $(+2w)$ wave function are quite similar to those obtained from O^{-2}(MgO). Also, the results of the three parameters F^{-1}(free) are quite similar to those obtained from F^{-1}(H.F.).

In view of these observations $\langle r^{-3} \rangle$ of F^{-1}(H.F.) was used when γ_∞ for F^{-1}(free) and $F^{-1}(3.7)$ was calculated; similarly $\langle r^{-3} \rangle$ of $O^{-2}(+2w)$ was used in the calculation of γ_∞ of O^{-2}(MgO).

As can be seen in Table I, γ_∞ of $F^{-1}(3.7)$ is $\approx 20\%$ smaller than F^{-1}(free). The reduction for the contracted $Cl^{-1}(x)$ is much larger. $F^{-1}(3.7)$ corresponds to a

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[22] E. G. Wikner, W. E. Blumberg, and E. L. Hahn, Phys. Rev. **118**, 631 (1960).

[23] C. H. Townes, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 38, see Table 9.

[24] D. A. Jennings, W. H. Tanttila, and O. Kraus, Phys. Rev. **109**, 1059 (1958).

[25] D. I. Bolef and M. Mernes, Phys. Rev. **114**, 1441 (1959).

[26] H. Kawamura, E. Otsuka, and K. Ishiwatari, J. Phys. Soc. (Japan) **11**, 1064 (1956).

[27] E. Otsuka and H. Kawamura, J. Phys. Soc. (Japan) **12**, 1071 (1957).

[28] T. P. Das (private communication) has shown that an important part, of the heretofore thought of squeezing effect, is indeed a charge effect.

[29] E. Otsuka, J. Phys. Soc. (Japan) **13**, 1155 (1958).

[30] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).

[31] R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959).

[32] S. Kaneko, J. Phys. Soc. (Japan) **14**, 1600 (1959).

[33] R. M. Sternheimer, Phys. Rev. **107**, 1565 (1957).

[34] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

contraction of F^{-1}(free) with a scale factor of ~1.03, while 1.132 was used for $Cl^{-1}(x)$. Judging from the fluorine results, the contraction in $Cl^{-1}(x)$ is probably too large. Thus, γ_∞ for the contracted chlorine wave function is still larger than the apparent experimental result. This would probably also be true for Br^{-1} and I^{-1} where -100 and -180 are obtained for γ_∞.[13] The large changes that occur when contracted wave functions are used point out the importance of calculating wave functions for the negative ions in their actual environment. Table II contains the results of calculations of γ_∞ for several positive ions and Kr. These results combined with previous calculated results[7,11–15] enable γ_∞ of almost any closed shell ion to be interpolated. Calculations for ions with half-filled shells (^6S states) are done in a manner similar to the closed-shell ion calculations. This is because the electrons of the ^6S state ion occupy all the orbital levels with parallel spins and the perturbations are spin independent. The wave functions for Mn^{+2} and Fe^{+3} have been calculated by Watson.[35]

As pointed out previously[12] there are large differences between γ_∞'s calculated from H. and H.F. wave functions even for the positive ions. However, the difference becomes smaller as the ion becomes more positive. Thus, by comparing the result of -6.97 for Ga^{+3}(H.F.) with -8.75 for Ga^{+3}(H.),[13] one would expect $\gamma_\infty = -11$ for In^{+3}(H.F.). The small result for Kr(H.F.) corroborates the statements in reference 12 asserting that the experimental antishielding factors obtained from Rb halides and Cs halides would be in agreement with theoretical calculations if H.F. wave functions were used in the calculations.

Some of these results have already been used.[19,20] Perhaps the results for In^{+3} will be useful for understanding the origin of q in the metal.[36] If eQq/h were measured for In in In_2O_3 and combined with the angular distribution measurements[37] of Cd^{111} in In_2O_3 along with the antishielding factor of the two,[38] one could get an approximate value of Q of this excited state of Cd.

eQq/h for the excited nuclear state of iron, Fe^{57m}, in Fe_2O_3 has been measured by Kistner and Sunyar[39] to be -5.6 ± 1.4 Mc/sec. Within the framework of the ionic model, one obtains Q by knowing eQq/h and calculating q from Eq. (1):

$$q = (1-\gamma_\infty) \sum_i e_i \left(\frac{3\cos^2\theta_i - 1}{r_i^3} \right), \tag{1}$$

where the sum is over all the ions in the lattice. Using a program developed by Bersohn,[16] the lattice sum was found to be $+7.48 \times 10^{12}$ esu/cm^3.

To eliminate many of the effects of the higher induced moments[12] in the O^{-2} ion, Q^{57m} was obtained from the ratio of eQq/h of Fe^{57m} to that measured for Al^{27} in Al_2O_3. Thus,

$$\frac{(eQq/h)_{57m}}{(eQq/h)_{27}} = \frac{(q)_{Fe_2O_3} Q^{57m}}{(q)_{Al_2O_3} Q^{27}}. \tag{2}$$

The values used for γ_∞, q, and Q^{27} are in footnote 40. It should be noted Hartree-Fock wave functions were used to calculate γ_∞. The value obtained is $Q^{57m} = -0.81 \times 10^{-24}$ cm^2.

Independently, Bersohn[41] has obtained a value for Q^{57m} and quotes for his most reliable determination $Q^{57m} = -0.19 \times 10^{-24}$ cm^2. This is obtained from Eq. (2). To do this he assumes the lattice sum in Eq. (1) to be the same in Fe_2O_3 as for Al_2O_3 except for a small scaling factor (the ratio of the unit cell dimensions cubed). However, the internal coordinates of the ions in Fe_2O_3 are not the same as in Al_2O_3 and the lattice sum used to obtain this value is too large by a factor of 4.23.[42]

It is interesting to note that the sum in Eq. (1) is quite sensitive to the internal coordinates and well within the error quoted for the x-ray results[40] q goes through zero and one can obtain a positive value for Q^{57m}.[43] A redetermination of the parameters in Fe_2O_3 would be useful.

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[35] R. E. Watson, Phys. Rev. **118**, 1036 (1960); and Technical Report No. 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, June 15, 1959 (unpublished).

[36] R. R. Hewitt and W. D. Knight, Phys. Rev. Letters **3**, 18 (1959).

[37] For a review of angular distribution work see: E. Heer and T. B. Novey, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1959).

[38] The extrapolated value for γ_∞ of Cd^{+2} (H. F.) is -15.

[39] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters 4, 412 (1960).

[40] R. V. Pound, Phys. Rev. **79**, 685 (1950) measured $eQq/h = 2.393$ Mc/sec for Al^{27} in Al_2O_3. Burns in reference 14 calculated, from Hartree-Fock wave functions, a value of -2.31 for γ_∞ of Al^{+3}. Bersohn in reference 16 quotes a value for the lattice sum in Al_2O_3 $+37.3 \times 10^{12}$ esu/cm^3 which has been checked and found correct by the authors. H. Lew and G. Wessel, Phys. Rev. **90**, 1 (1953) obtain a value for Q of $+0.149 \times 10^{-24}$ cm^2 for Al^{27}. The structure data was taken from L. Pauling and S. B. Hendricks, J. Am. Chem. Soc. **47**, 781 (1925).

[41] R. Bersohn, Phys. Rev. Letters 4, 609 (1960).

[42] One can do the calculation by dividing eQq/h by the result obtained from Eq. (1). This is probably less accurate. However, if one does, $Q^{57m} = -1.4 \times 10^{-24}$ cm^2 is obtained (compared to -0.33×10^{-24} cm^2 in reference 41).

[43] The parameter describing the positions of the O^{-2} ions is $u = 0.292 \pm 0.007$ (see reference 40). As u decreases, Q^{57m} gets to be a larger negative number until at $u = 0.289$ it becomes infinite and then positive for smaller u. For $u = 0.285$ $Q^{57m} = +0.56 \times 10^{-24}$ cm^2.