

***Ab initio* Determination of $^{57}\text{Fe}^m$ Quadrupole Moment from Mössbauer Data**

K. J. Duff

*Department of Physics, University of Wollongong, Wollongong, New South Wales 2500, Australia, and
Department of Physics, State University of New York at Albany, Albany, New York 12222*

and

K. C. Mishra and T. P. Das

Department of Physics, State University of New York at Albany, Albany, New York 12222

(Received 29 December 1980)

A new determination of the $^{57}\text{Fe}^m$ quadrupole moment has yielded the value 0.082 b, which is only *half* of the currently accepted value. The procedure combined first-principles calculation of the field gradients at the Fe nucleus in FeCl_2 and FeBr_2 molecules with published quadrupole splittings for those molecules trapped in rare-gas matrices. The field gradients are strongly influenced by iron $3p$ covalency.

PACS numbers: 21.10.Ky, 27.40.+z, 33.45.+x

The interpretation of $^{57}\text{Fe}^m$ quadrupole interaction data from Mössbauer measurements requires the comparison of a measured quadrupole splitting with that calculated from the product of the nuclear quadrupole moment Q and the electric field gradient (EFG) as deduced from an assumed electronic structure. In ionic solids, where much of the interpretative effort has been concentrated, several effects contribute to the field gradient: asymmetric charge distributions indigenous to the iron site, point charge and higher multipoles surrounding the iron, Sternheimer shielding and anti-shielding effects,¹ orthogonality requirements for orbitals centered on different sites, covalent charge transfer, and self-consistency. The history of the determination of the $^{57}\text{Fe}^m$ quadrupole moment from calculated field gradients is lengthy²⁻⁵ because, until recently, there was no single computational system capable of handling all effects simultaneously. The availability of large-scale computer codes for the calculation of the wave functions and properties of all electrons in small clusters of atoms has improved this situation. We report here a determination of Q from calculations for the molecules FeCl_2 and FeBr_2 trapped^{6,7} in Ar and Xe. Our deduced value of Q is 0.082 b, approximately one half of the currently accepted value for this quantity. This shift in the value for Q will have a marked effect on the field gradients determined in other materials from measurements of the quadrupole interaction energies, essentially doubling them as compared with those obtained by use of the most recent quadrupole moment.⁵ The understanding of these field gradients, especially in molecular and ionic crystal systems, will need the important features of the present electronic structure calculation.

Several lines of evidence indicate that the influence of the rare-gas matrix on the iron halide molecules is weak, although a contrary suggestion⁸ has been made for FeCl_2 . (a) Infrared spectroscopy of FeCl_2 in the gas phase⁹ and in the rare-gas matrix¹⁰ shows that in both cases the molecule is linear. (b) Since the vibrational frequency of a molecule is related¹¹ through the force constants to the EFG, any strong perturbation of the electronic structure which is capable of affecting the EFG at the Fe site in FeCl_2 would be revealed by a shift in the vibrational frequency. Several metal di-halides have been studied in the vapor phase⁹ and also in the Ar-matrix isolation.¹⁰ In all cases the shift in the asymmetric stretching frequency (ν_3) between gas phase and Ar-matrix isolation is small. (c) Any strong perturbation by the rare-gas matrix would surely be expected to depend on the rare-gas host. However, the quadrupole splitting⁷ for FeCl_2 is unaffected by a change of matrix from Ar to Xe. (d) *Ex post facto*, we find very good agreement between the quadrupole moment we calculate from FeCl_2 and that which we calculate from FeBr_2 . If the Ar matrix was strongly affecting the trapped molecules, the shift in EFG would be dependent on which molecule was trapped, and we should not then obtain agreement between the two. We believe points (a)–(d) provide strong evidence that the properties of the trapped ferrous di-halide molecules are those of the corresponding gas-phase molecules, and accordingly we have assumed iron-halogen internuclear distances to be those of the free molecules,¹² namely 2.17 and 2.307 Å for FeCl_2 and FeBr_2 , respectively. However, to test the sensitiveness of the EFG to the internuclear separation, a change in which can be

considered to be a manifestation of environmental effects on the molecules, we have repeated the molecular calculations for a Fe-Cl distance of 2.16 Å, the lower limit of the experimental distance. One does not expect a change larger than this because this would lead to a significant change in ν_3 which is not observed.¹⁰ Also, the difference between Fe-Cl distance in FeCl₂ and the drastically different Fe₂Cl₆ crystal is 0.05 Å and this also suggests that 0.01 Å can be considered as a reasonable upper limit for the difference between Fe-Cl distances for the FeCl₂ molecule when it is free and in a rare-gas matrix.

Self-consistent-field-unrestricted-Hartree-Fock (SCF-UHF) molecular wave functions for FeCl₂ and FeBr₂ were determined by use of the POLYATOM¹³ system of computer programs. This system utilizes analytic expansions in contracted Gaussian¹⁴ orbitals, evaluating all integrals (including all multicenter integrals) analytically. The electric-field-gradient contributions at the ⁵⁷Fe^m nucleus were calculated for each occupied molecular orbital, and for the ligand nuclear charges, and the various contributions are displayed in Table I. Orbitals attributed to a particular kind of site are those molecular orbitals for which the dominant expansion coefficients are for basis functions centered on that kind of ion. This necessarily means, for example, that contributions listed as referring to halogen orbitals contain components arising from an admixture of iron orbitals. Such an admixture would produce, in addition to a charge density local to the halogen site, a local charge density on the iron site and a nonlocal¹⁵ charge density arising from the product of one iron-centered function and one halogen-centered function. We have not performed the cumbersome task of separating such contributions. In the past such a separation has been traditional because the approximate method of determining the field gradient by the use of Sternheimer shielding factors has required it.⁴ The use of

shielding factors would be incorrect here because the process of iteration to self-consistency already contains shielding effects within it.

To show that the shielding mechanisms are properly incorporated in the present methodology, and thus to add confidence to our value for the ⁵⁷Fe^m quadrupole moment, we have performed a number of special calculations. In each of these an isolated Fe²⁺ ion was placed between bare halogen nuclei with the internuclear separations the same as in the corresponding ferrous dihalide molecule. In each case the POLYATOM¹³ system was used to perform a perturbation calculation (that is, no iteration). In the first calculation, the Fe²⁺ ion was assumed to be in the state most closely approximating its state in the molecule, namely, it is nonspherical, the nonsphericity occurring because the minority-spin state $3d_{xy}$ is occupied while all the other minority d states are empty. In the second calculation, an artificial spherical Fe²⁺ has been constructed by populating all minority-spin d states with one fifth of an electron. This set of two calculations was carried out with both chlorine and bromine nuclear charges as sources. The difference between the first and second calculations of each set provides the contributions from the single nonspherical d state, including shielding by s and p electrons. On dividing the sum of the s and p shielding contributions by the d contribution we arrive at a value for the Sternheimer shielding parameter¹ R of 0.042. While the methodology does not correspond directly with that of the recent many-body calculation⁵ on the field-gradient and shielding effects in Fe²⁺ ion, our result is reasonably close to the result of 0.084 obtained therein, and quite different from the value 0.32 frequently used in the past which has been shown⁵ to be incorrect. The second calculations for the artificial Fe²⁺ ion for the cases of chlorine and bromine nuclear charges provide values of the antishielding factors γ_∞ for the cases, which are

TABLE I. Electric-field-gradient contributions in FeCl₂ and FeBr₂ molecules. All contributions are in units of 10¹⁴ esu/cm³.

| | s states | $2p$ | Iron orbitals | | Total | Halogen orbitals | Total electronic | Halogen nuclear charges | Total | Quadrupole splitting ^a (mm/s) | Q (b) |
|-------------------|------------|------|---------------|--------|---------|------------------|------------------|-------------------------|--------|--|---------|
| | | | $3p$ | $3d$ | | | | | | | |
| FeCl ₂ | 1.36 | 1.23 | 1.13 | -96.39 | -92.66 | 101.18 | 8.50 | -31.93 | -23.45 | 0.63 ± 0.02 | 0.086 |
| FeBr ₂ | 1.68 | 3.56 | -11.11 | -97.33 | -103.19 | 122.59 | 19.40 | -54.74 | -35.34 | 0.86 ± 0.02 | 0.078 |

^aRefs. 6 and 7.

found to be -8.9 and -9.5 , respectively, in good agreement with that determined previously¹⁶ in Hartree-Fock calculations.

Inspection of the entries in Table I shows that, except for the iron $3p$ contributions, there is rough agreement in sign and size between the entries for FeCl_2 and FeBr_2 . The reason for the exception for the iron $3p$ contributions lies in a combination of two effects: Covalent charge transfer essentially affects only the outermost iron orbitals, that is, the $3p$ and $3d$ states, and of these the $3p$ states have a larger value of r^{-3} than the d states by a factor of about 11. To demonstrate that, for the field-gradient calculations, the $3p$ states are the most sensitive to the details of covalency effects, we performed two additional perturbation-model calculations. In the first of these an isolated Fe^{2+} ion was subjected to the potential of two isolated Cl^- ions. In the second, the wave functions of the isolated Fe^{2+} ion were calculated in the potential produced by the SCF wave functions of the molecule. In neither of these calculations was the Fe^{2+} permitted to form molecular orbitals. The various contributions to the field gradient for the two cases, together with the difference between them, are shown in Table II.

Line 3 of Table II shows that it is the field-gradient contributions from the $3p$ state that are most strongly affected by the potential distortion induced by the covalent charge transfer. In addition to this aspect of the sensitiveness of $3p$ contributions to covalency, a substantial part of the contributions from molecular orbitals referred to as halogen orbitals (because the major component involves halogen-atom orbitals) is represented by iron $3p$ atomic-orbital contributions. The net contribution from the $3p$ atomic-orbital contributions due to covalency effects is thus substantially larger than the small contribution in Table I referred to as $3p$ -type molecular-orbital contribution, and is indeed of comparable importance to the $3d$ contribution. Previous determina-

tions^{2,5} of the $^{57}\text{Fe}^m$ quadrupole moment have addressed the question of $3d$ covalency, but, in addition, the present results indicate that it is essential to include $3p$ covalency. In particular, determinations relying on orthogonalization¹⁷ of metal and ligand orbitals as the sole mechanism of molecular-orbital formation cannot be expected to give satisfactory results.

The quadrupole moment for $^{57}\text{Fe}^m$ as deduced from the SCF-UHF wave functions is shown in Table I for each molecule. These have been deduced with use of the experimental quadrupole splittings recorded^{6,7} for the rare-gas-matrix-isolated monomeric molecules. The results for FeCl_2 and FeBr_2 are, respectively, 0.086 and 0.078 b, in close agreement with each other. In deciding on the confidence limit of our result for the quadrupole moment, a number of considerations are involved. First, there is the many-body correlation effect. A consideration of many-body effects in calculations on the local electronic contribution¹⁸ to the field gradient in Fe^{2+} ion and related systems¹⁹ and on the antishielding factor in Fe^{3+} ion²⁰ suggests no more than about 2% effect due to this source. The influence of environmental effects on the EFG in the molecules can be gauged from the variation of about 3% in the EFG that we have found, for a 0.5% change in the internuclear distance in FeCl_2 . In addition there are small but significant error bars in the experimental coupling constants in the two molecules. From these considerations, we suggest that the quadrupole moment of $^{57}\text{Fe}^m$ be taken to be the mean of our results in FeCl_2 and FeBr_2 with a tolerance of 10%.

Prior expectations have been that the $3d$ electrons, especially the fractional population of the minority spin half-shell, would be the main contributor² to Fe field gradients. Important as such terms are, we have found here that $3p$ electrons also make a major contribution through direct charge transfer, potential distortion, and nonlocal charge distributions. We have found consis-

TABLE II. Field-gradient contributions (in units of 10^{14} esu/cm³) for an isolated Fe^{2+} ion subjected to two potentials.

| Potentials | s states | $2p$ | $3p$ | $3d$ | Total |
|--|------------|------|--------|--------|---------|
| Two isolated Cl^- ions + Fe^{2+} | | | | | |
| intraionic | 1.65 | 0.91 | -17.72 | -91.11 | -106.26 |
| SCF molecule | 1.26 | 1.26 | 3.69 | -85.70 | -79.45 |
| Line 2 - line 1 | -0.40 | 0.36 | 21.41 | 5.41 | 26.80 |

tency between the calculations for FeCl_2 and FeBr_2 . Our findings imply that the future interpretation of field gradients will be more difficult than previously supposed, but one thereby gains an independent caliper of $3p$ charge distributions.

This work was partially supported by the U. S. National Institutes of Health under Grant No. GM-2523003.

¹R. M. Sternheimer, Phys. Rev. A **6**, 1702 (1972), and Phys. Rev. **130**, 1423 (1963).

²R. Ingalls, Phys. Rev. **133**, A787 (1964).

³R. Bersohn, Phys. Rev. Lett. **4**, 609 (1960); R. R. Sharma and T. P. Das, J. Chem. Phys. **41**, 3581 (1964); G. Burns, Phys. Rev. **124**, 524 (1961); J. O. Artman, A. H. Muir, and H. Wiedersich, Phys. Rev. **173**, 337 (1968).

⁴R. R. Sharma, Phys. Rev. Lett. **26**, 563 (1971); R. R. Sharma and B. N. Teng, Phys. Rev. Lett. **27**, 679 (1971); D. Sengupta, J. O. Artman, and G. A. Sawatzky, Phys. Rev. B **4**, 1484 (1971); A. C. Beri, T. Lee, R. M. Sternheimer, and T. P. Das, Hyperfine Interact. **4**, 509 (1978).

⁵S. N. Ray and T. P. Das, Phys. Rev. B **16**, 4794 (1977) have obtained the value of 0.15 b which was derived from quadrupole-coupling data in ionic ferrous compounds with use of many-body calculations of the field gradient in free Fe^{2+} ion and an approximate analysis of convalency effects. H. H. Bolotin, A. E. Stuchberg, K. Amos, and I. Morrison, Nucl. Phys. **A311**, 75 (1978) have obtained 0.177 b from nuclear-

structure calculations.

⁶T. K. McNab, D. H. W. Carstens, D. M. Gruen, and R. L. McBeth, Chem. Phys. Lett. **13**, 600 (1972).

⁷F. J. Litterst, A. Schichl, and G. M. Kalvius, Chem. Phys. **28**, 89 (1978).

⁸H. Shechter, J. G. Das, M. Mor, R. Ingalls, and S. Bukshpan, Phys. Rev. B **14**, 1876 (1976).

⁹G. E. Leroi, T. C. James, J. T. Hougen, and W. Klemperer, J. Chem. Phys. **36**, 2879 (1962).

¹⁰K. R. Thompson and K. D. Carlson, J. Chem. Phys. **49**, 4379 (1968); R. A. Frey, R. D. Werder, and Hs. H. Günthard, J. Mol. Spectrosc. **35**, 260 (1970).

¹¹A. A. Anderson, N. C. Handy, and R. G. Parr, J. Chem. Phys. **50**, 3634 (1969).

¹²N. G. Rambidi and E. Z. Zazorin, High Temp. **2**, 636 (1964); E. Vajda, J. Tremmel, and I. Hargittai, J. Mol. Struct. **44**, 101 (1978).

¹³J. W. Moskowitz and L. C. Snyder, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer, III (Plenum, New York, 1977).

¹⁴T. H. Dunning, Jr., and P. J. Hay, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer, III (Plenum, New York, 1977).

¹⁵See, for example, Beri *et al.*, Ref. 4.

¹⁶R. Ingalls, Phys. Rev. **128**, 1155 (1962) found $\gamma_\infty(\text{Fe}^{2+}) = -10.6$; R. M. Sternheimer, Phys. Rev. **130**, 1423 (1963) found $\gamma_\infty(\text{Fe}^{3+}) = -9.14$.

¹⁷Sharma, Ref. 4.

¹⁸Ray and Das, Ref. 5.

¹⁹S. N. Ray, T. Lee, and T. P. Das, Phys. Rev. A **8**, 1748 (1973); J. E. Rodgers and T. P. Das, Phys. Rev. A **12**, 1168 (1975); J. E. Rodgers, R. Ray, and T. P. Das, Phys. Rev. A **14**, 543 (1976).

²⁰S. N. Ray, T. Lee, and T. P. Das, Phys. Rev. A **9**, 93 (1974).

Pion Charge-Exchange Reaction as a Probe of Isovector Monopole Resonances

J. David Bowman and Mikkel B. Johnson

Los Alamos National Laboratory, Los Alamos, New Mexico 87544

and

J. W. Negele

Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 10 March 1981)

We argue that the nuclear giant isovector monopole resonance should be observable with pion charge-exchange reactions (π^- , π^0) in the energy region close to the (3, 3) resonance.

PACS numbers: 24.30.Cz, 25.80.+f

Giant resonances are fundamental to our understanding of nuclear collective motion. Monopole or breathing modes involve periodic compression and expansion of the proton and neutron densities in the interior coupled to oscillations in the dis-

tribution of nucleons in the surface. Recent exploration of the systematics of isoscalar monopole resonances has provided valuable insight into the compression modulus of nuclear matter and the interplay of bulk compression with surface dy-