Evaluation of the ^{57m}Fe Quadrupole Moment from Hartree-Fock Calculations*

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Two theoretical evaluations of ^{57m}Fe quadrupole moment (Q), based on different formalisms, namely the Hartree-Fock theory and the Linearized Augmented Plane Wave method have yielded results differing by a factor of two. In both cases, Q was obtained from experimental quadrupole interaction frequencies through investigation of the Electric Field Gradients at the nuclear site of the ^{57m}Fe probe. It is the purpose of the present work to reexamine the earlier Hartree-Fock approach. In particular, the earlier model is extended through a more realistic description of the environment of ^{57m}Fe in the respective experiments, as well as through inclusion of electron correlation effects.

In Hyperfine Interaction experiments, no nuclear probe has been used more frequently than the isotope ^{57m}Fe. Extraction of information about the electronic environment of the ^{57m}Fe probe from quadrupole interaction data requires the knowledge of the ^{57m}Fe quadrupole moment (Q).

This quantity, however, has been the subject of a long-standing controversy. While it had been previously assumed to be in the range of 0.15 to 0.28 b, a Hartree-Fock calculation by Duff, Mishra and Das [1] yielded the smaller value $Q = 0.082$ b. The authors analyzed Mössbauer experiments dealing with FeX_2 (X = Cl, Br) embedded in a solid Ar matrix. The value of the ^{57m}Fe quadrupole moment was deduced from measured quadrupole interaction frequencies using theoretical Electric Field Gradients (EFGs) as found at the nuclear site of the ^{57m}Fe probe. The small value of $Q(^{57m}Fe)$ resulting from this treatment was subsequently confirmed by nuclear theory [2].

The most recent theoretical effort directed at the evaluation of the ^{57m}Fe quadrupole moment [3] contradicted the earlier work, yielding a value of $Q(^{57m}Fe) = 0.16$ b and thus restoring the original size estimate. This reassessment was based on the interpretation of experimental quadrupole splitting data in a large number of compounds, using the Linearized Augmented Plane Wave band structure method.

Thus, results relying on two different theoretical procedures are seen to be in a conflict with each other which demands resolution.

The work presented here is aimed at an extension of the former Hartree-Fock approach toward the solution of the $Q(^{57m}Fe)$ problem, and particularly at a careful reexamination of the hypotheses underlying the earlier work. In this way, it is hoped, a reconciliation between the two differing views can be achieved eventually.

The guidelines for the present calculation can be summarized as follows. Special emphasis was put on:

(i) The choice of suitable basis sets, i.e. basis sets which can be expected to describe local electronic properties reliably. This is of particular relevance for the Fe basis.

(ii) Incorporation of possible effects due to the solid Ar matrix.

(iii) Inclusion of electron-electron correlation effects.

Neither (ii) nor (iii) was taken into account in the earlier Hartree-Fock calculation, where the units FeX_2 (X = Cl, Br) were treated as free molecules and the influence of electronic correlation on the EFG was neglected.

For the Fe basis set selection, the following criterion was adopted: This basis set is required to give an adequate representation of wave function related properties of the Fe atom. The most important one of these is, in the context of the problem under study, the

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Table 1. Comparison of $\langle 1/r^3 \rangle$ expectation values at the nuclear site of Fe in units e/a_0^3 as obtained from the basis set chosen in this work and from numerical calculations.

Quantity	Atomic HF calculation	Standard value
$\langle 1/r^3 \rangle$ (2p)	468.26	468.58
$\langle 1/r^3 \rangle$ (3p)	52.04	55.71
$\langle 1/r^3 \rangle$ (3d)	4.93	4.86

Table 2. Values of the V_{zz} component in units of e/a_0^3 for $FeCl_2$ and $FeBr_2$ as obtained for a sequence of basis sets.

Quantity	Composition of basis set (7/6/4)	(7/6/5)	(7/6/5/1)	Experiment
V_{zz} ($FeCl_2$)	0.598	0.596	0.578	
V_{zz} ($FeBr_2$)	0.902	0.796	0.791	
R	1.508	1.334	1.368	1.36 (0.04)

expectation value $\langle 1/r^3 \rangle$ at the nuclear site of the atom which is for every atomic orbital directly proportional to the V_{zz} component of the EFG tensor due to that orbital. We chose a (7/5/5/1) basis set [4] (consisting of 7 s-, 6 p-, 5 d- and 1 f- functions), comparing the $\langle 1/r^3 \rangle$ expectation values derived for the Fe 2p, 3p and 3d shells to numerical standard values for these quantities [5]. Particular emphasis was placed on a satisfactory reproduction of the 3d contribution. From Table 1 it is obvious that the basis set chosen allows for a good reproduction of the 2p and 3d contributions to V_{zz}. The somewhat larger deviation found for the 3p shell can be tolerated since the effect of the Fe p shells on the EFG at the nuclear site of Fe is expected to be very small as compared to the Fe 3d shell.

Similar considerations were followed in selecting basis sets for Cl [6] and Br [7].

As a test for the adequacy of our approach, we computed the ratio R of the experimental quadrupole interaction frequencies observed for $FeBr_2$ and $FeCl_2$ which equals the ratio of the V_{zz} components at the nuclear site of the Fe atom for $FeBr_2$ and $FeCl_2$, respectively. The measured value is $R_{exp} = 1.36$ (0.04) [8, 9].

A sequence of three calculations was carried out, using basis sets of increasing complexity. The theoretical and measured ratios, summarized in Table 2, are in very good agreement. It should be noted that the deviation between theory and experiment decreases with increasing basis set complexity.

In reliance on Hund's Rule, a quintet spin state was assumed in all these calculations, corresponding to a multiplicity of five. However, in view of the strong dependence of the EFG on the system's spin state, it is essential to test this assumption. Thus, a comparative study of total energies of the $FeCl_2$ molecule as spin singlet, triplet and quintet was carried out. As is obvious from Table 3, these results reflect a strong preference of the quintet spin state which clearly exhibits the lowest energy in this series.

Table 3. Comparison of different spin states for $FeCl_2$.

Spin State	Total Energy of $FeCl_2$ (in units keV)
Singlet	–59.319
Triplet	–59.317
Quintet	–59.326

Table 4. The dominating shell contributions to the V_{zz} component in units of e/a_0^3 for $FeBr_2$ and $FeCl_2$.

	Fe(2p)	Fe(3p)	Fe(3d)	Halogen orbitals	Halogen nuclear charges
$FeCl_2$	0.275	0.066	2.805	–3.493	0.980
$FeBr_2$	0.295	0.104	2.894	–4.105	1.690

For both, $FeBr_2$ and $FeCl_2$, we investigated the contributions of the individual molecular orbitals to the total EFGs in an effort to account for the physical origin of the difference between both EFGs. Table 4 lists the dominating V_{zz} contributions for both, $FeBr_2$ and $FeCl_2$. As expected, the main differences between the V_{zz} values for $FeBr_2$ and $FeCl_2$ are found at the entries of the Halogen orbitals and the Halogen nuclear charges. Only the Fe(3p) shells appear to be substantially influenced by covalency effects. These effects are consistently stronger for $FeBr_2$ than for $FeCl_2$.

We accounted for the influence of the Ar matrix on the EFGs of $FeBr_2$ and $FeCl_2$ by adopting a cluster model and enclosing both molecules into a cage consisting of 12 Ar atoms. The effect of possible Ar lattice distortion due to the embedded molecule was examined performing a geometry optimization where the fcc structure of the undistorted Ar lattice was used as initial geometry. As a consequence, contractions of the distance between the central Fe atom and Ar atoms situated off the equatorial plane were observed. This in turn was found to induce an asymmetry of the configuration which gives rise to a finite η parameter, contradicting the experimental finding of vanishing η [8, 9]. Thus, in all subsequent geometry optimizations, fcc geometry of the surrounding Ar lattice was maintained as a geometric constraint (see Figure 1).

In an additional geometry optimization effort, the orientation of the $FeCl_2$ molecule within an Ar cage

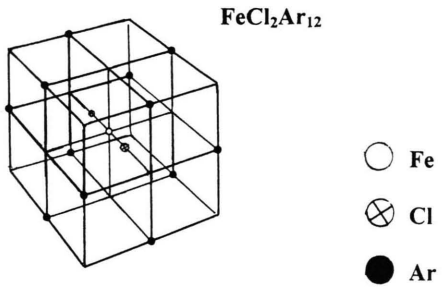

Fig. 1. The $FeCl_2Ar_{12}$ model adopted in the calculations described in the text.

was varied systematically. The position indicated in the figure, corresponding to D_{4h} symmetry of the cluster as a whole and ensuring maximum distance between the Cl atoms and the atoms of the cage, emerges as the most stable one.

Subsequently, the fcc lattice parameter was optimized in a series of computations for both systems, $FeCl_2Ar_{12}$ and $FeBr_2Ar_{12}$. We calculated the ratio R between the $FeBr_2$ and the $FeCl_2$ quadrupole interaction frequencies using two basis sets of different extensions for the Fe atom, namely (7/5/3) : "Basis A" and (7/6/3) : "Basis B". This resulted in a finding of R = 1.43 for Basis A and R = 1.38 for Basis B. The result derived employing the more flexible basis is obviously in better agreement with the observed value R = 1.36 (0.04).

To arrive at an overall conclusion with regard to the ^{57m}Fe quadrupole moment, we subjected the system $FeCl_2Ar_{12}$ to a calculation using the most flexible Fe basis set employed in this work whose contraction pattern is (7/6/5/1). A considerable expansion of the Ar lattice was found, the cell edge increasing from its equilibrium value of 5.32 Å [10] to 7.01 Å. For the EFG at the nuclear site of the Fe atom, we obtain a V_{zz} component of 0.572 e/a_0^3 with V_{xx} and V_{yy} components of –0.286 e/a_0^3.

This is in very close proximity of the V_{zz} value obtained for the free $FeCl_2$ molecule (see Table 2). The impact of the Ar lattice on the EFG parameters appears to be very slight in the framework of our model. However, in view of the very considerable sensitivity of the EFG on the FE-X distance, it has to be ascertained that the distance D chosen in these calculations – D = 2.17 Å, equal to the experimental distance found for the free $FeCl_2$ molecule – is the correct one. We did this by performing an energy optimization of the parameter D for the $FeCl_2$ molecule inside the Ar cage. Through this inspection we found the energy minimum at the molecular value D = 2.17 Å, in agreement with our assumption.

Table 5. EFG at the Fe site of $FeCl_2Ar_{12}$ by various Hartree-Fock based methods (HF = Hartree-Fock, MP2 = Möller-Plesset perturbation theory at second order, CCD = Coupled Cluster calculation, see text).

Procedure	V_{xx}	V_{yy}	V_{zz}
HF	–0.286	–0.286	0.572
MP2	–0.275	–0.275	0.551
CCD	–0.278	–0.278	0.557

The effect of electron-electron correlation was taken into account through application of two different procedures: A perturbation theory treatment on the level of Möller-Plesset theory at second order (MP2) and a coupled cluster calculation, using double substitutions from the Hartree-Fock determinant (CCD). This yielded in both cases EFG eigenvalues of somewhat reduced magnitude as compared with the Hartree-Fock treatment, as can be seen from Table 5.

Thus, correlation effects cause a small but noticeable reduction of our result for the quantity V_{zz}. The two different approaches chosen lead to very similar values. Incorporation of electron correlation is seen to diminish the charge on the Fe atom from q(Fe) = 1.04 (Hartree-Fock calculation) to q(Fe) = 0.97 (CCD calculation). The physical reason for the observed impact of electron correlation on the EFG lies in a rearrangement of the beta ("spin down") electron system as one incorporates many-body effects into the Hartree-Fock model. While the 3d beta electron of Fe was found from the Hartree-Fock computation occupying a D_{-2} orbital, corresponding to a strongly positive contribution to the V_{zz} component of the EFG at the Fe nucleus, a strong admixture of D_{-1} angular character, associated with a negative contribution to the V_{zz} component, is found for the Fe 3d-beta electron from the Post-Hartree-Fock calculations performed.

On the basis of the CCD value for the V_{zz} component, we derive a quadrupole moment for the ^{57m}Fe nucleus of $Q(^{57m}\text{Fe})$ = 0.11. This outcome moves the quadrupole moment computed by Duff et al. ($Q(^{57m}\text{Fe})$ = 0.086) for $FeCl_2$ somewhat towards the finding of Dufek et al. ($Q(^{57m}\text{Fe})$ = 0.16). Still, Hartree-Fock based theory is seen to tend systematically towards smaller values than the Linearized Augmented Plane Wave treatment. Further refinement of both approaches may remove the remaining discrepancy between the two results.

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