The nuclear quadrupole moment of $^{57}$Fe from microscopic nuclear and atomic calculations

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The nuclear quadrupole moment of the $I^\pi=3/2^-$ excited nuclear state of $^{57}$Fe at 14.41 keV, important in Mössbauer spectroscopy, is determined from the large-scale nuclear shell-model calculations for $^{57}$Fe and also from the electronic ab initio and density functional theory calculations including solid state and electron correlation effects for the molecules Fe(CO)$_5$ and Fe(C$_3$H$_2$)$_2$. Both independent methods yield very similar results. The recommended value is 0.16(1) eb. The NQM of the isomeric $^{10+}$ in $^{55}$Fe has also been calculated. The new value (0.5 eb), consistent with the perturbed angular distribution data, is by a factor of two larger than the currently recommended value.

21.10.Ky, 21.60.Cs, 31.15.Ar, 31.30.Gs, 76.80.+y, 27.40.+z

Mössbauer spectroscopy of $^{57}$Fe plays an important role in the structural determination of iron containing solid state compounds. In principle, the nuclear quadrupole moment (NQM) of the isomeric $I=3/2$ state in $^{57}$Fe can be determined from Mössbauer data; however, the analysis requires the calculation of the electric field gradient (EFG). As these atomic calculations are quite involved, studies employing different methods arrived at quite distinct results: the values of NQM in the range from −0.19 to +0.44 eb have been reported. This quite unsatisfying situation could also not have been settled by nuclear structure calculations of the NQM as calculations within the nuclear shell model, the most reliable tool for such studies, had to be performed in strongly truncated model spaces and with rather untested effective interactions. In recent years, decisive progress has been achieved in both the atomic calculations of the EFG and in nuclear shell model studies.

In 1995, Dufek and co-workers applied the density functional theory for a series of iron-containing solid state compounds. For $^{57}$Fe they obtained a NQM of 0.16 eb, in contradiction with the previously accepted value of 0.082 eb obtained from Hartree-Fock (HF) EFG calculations and from truncated nuclear shell-model calculations combined with the perturbed angular distribution data. In subsequent work, Su and Coppens obtained a NQM value of 0.12(3) eb using Sternheimer-corrected EFGs. In this Letter, we shall demonstrate that state-of-the-art nuclear and atomic physics calculations lead to the same NQM for the $^{57}$Fe isomeric state, settling a long-standing controversial issue.

We shall begin with the nuclear physics discussion. The nucleus $^{57}$Fe has two low-lying $3/2^-$ states which are experimentally split by only 353 keV. To describe the structure of such nearly degenerate states is quite demanding. Clearly, the large-scale shell model is the method of choice. Due to recent progress in programming and hardware development, modern shell-model calculations based on microscopic effective interactions can handle configuration spaces that were prohibitively large only several years ago. More specifically, modern diagonalization shell-model codes can now handle medium-mass nuclei ($A=50-60$) in the middle of the $pf$ shell in full $0\hbar\omega$ space. To put things in perspective, the shell-model calculations of the Utrecht Group, which were used in Ref. to extract the NQM of $^{57}$Fe, restricted the number of holes in the $f_{7/2}$ orbit to three.

Shell-model calculations depend crucially on two factors: the model space and the effective interaction. Our calculations have been performed using the code NATHAN. NATHAN has been developed in the $jj$-coupling scheme using quasispin formalism. We adopt a version of the code adapted to shared-memory parallel machines. For the two lowest $3/2^-$ levels, we assumed the truncated space (containing 8,120,105 $I^\pi=3/2^-$ states) in which maximally 6 nucleons were allowed to be excited from the $f_{7/2}$ orbital to the rest of the $pf$ shell. To test the convergence of our results, we have performed a full $pf$ shell calculation for the lowest $3/2^-$ state. This calculation includes 25,743,302 states ($\sim2\cdot10^{13}$ non-zero matrix elements) and is one of the largest shell-model diagonalization performed to date. For all adopted interactions, the results of the truncated and complete calculations are identical.

During the last few years, a considerable effort went into the development of effective interactions in the $pf$ shell. In this work three different effective interactions have been employed: KB3F, KB3G, and FDP6. The in-
interactions KB3F and KB3G are both reasonable attempts to correct the defects of the well-known KB3 interaction in the upper part of the pf-shell. They differ slightly in their collectivity of states around $^{58}$Ni. As far as $^{57}$Fe is concerned, KB3G is clearly the interaction of choice; it has been shown to be very successful in describing experimental data (including energy levels and electromagnetic properties) in the mass region $A=50-52$ and around $A=56$. The FPD6 interaction was originally fitted to the spectroscopic properties of $f_{7/2}$ nuclei and has since been extended to nuclei around the N=Z=28 shell closure. For the effective charges, we took the quadrupole charges 1.5e for protons and 0.5e for neutrons when calculating E2 transitions and moments, and the spin and orbital gyromagnetic factors $g_s=0.75g_{bare}$, $g_f^s=1.1\mu_N$, and $g_f^l=-0.1\mu_N$ for M1 transitions and moments, e.g. (4). We adopt the oscillator parameter $b = 1.01A^{1/6}$ fm.

Our shell-model calculations reproduce well the experimental level scheme of $^{57}$Fe. In particular, the low-lying $I^+=3/2^-$ doublet is predicted by theory. Experimentally, the energy difference between these states is 353 keV, while theoretically it is 526, 209, and 465 keV using the KB3F, KB3G, and FPD6 interactions, respectively. The third $3/2^-$ state appears much higher in energy, at about 1.6 MeV. Table I summarizes our shell-model results for the quadrupole and magnetic moments of the two lowest $3/2^-$ states in $^{57}$Fe. It is seen that these close-lying states in the doublet are predicted to have very different shapes and magnetic moments, i.e., their E2 and M1 moments have different signs. Consequently, even small changes in the shell-model interaction, hence in the coupling between these states, significantly impact theoretical predictions. We note that a convergence of the shell-model results is not reached if only three $f_{7/2}$ holes are allowed, as was done in the previous truncated calculations. For example, the value of the NQM of the $3/2^-$ state, $Q(3/2^-)$, obtained in such truncated calculations with the KB3G interaction, is 0.097 eb, as compared to the exact value of 0.064 eb.

In order to assess the sensitivity of the results on the adopted effective force, we computed overlaps between wave functions of the $3/2^-$ states obtained with the different interactions. It turned out that the spaces of the two lowest $3/2^-$ states in KB3F and KB3G are practically (up to 95%) the same. That is, both $3/2^-$ wave functions obtained with KB3F can be approximately derived from the $3/2^-$ doublet calculated with KB3G by simple rotation. This does not hold for KB3G and FPD6. Since FPD6 tends to excite particles to the $f_{5/2}$ shell rather than the $p_{3/2}$ shell (FPD6 puts the $f_{5/2}$ orbit too low at N=28), the contributions from higher-lying $3/2^-$ states amount to about 37%.

Due to the great sensitivity of the shell-model predictions caused by the not-very-well-controlled off-diagonal coupling between the $3/2^-$ doublet, the calculations need to be constrained by the available experimental data. To this end, we choose the magnetic moment of the $3/2^-$ state, which has been precisely determined experimentally, $\mu(3/2^-)=-0.1549(2)\mu_N$ Assuming that the “true” wave functions of the $3/2^-$ doublet are given by a simple rotation of the shell-model states,

$$|3/2^-\rangle = \alpha_1 |3/2^-;\text{SM}\rangle + \alpha_2 |3/2^-;\text{SM}\rangle,$$

one can determine the mixing amplitudes $\alpha_1$ and $\alpha_2$ ($\alpha_1^2 + \alpha_2^2 = 1$) by requesting that the measured value of $\mu(3/2^-)$ be reproduced. The results of such two-level mixing calculations are displayed in Table I. Contrary to the pure shell-model results, one obtains a satisfying agreement between KB3F and KB3G, and the data. In particular, the quadrupole moments predicted by these interactions are very similar, $Q(3/2^-)\approx0.17$ eb. The only serious difference is the sign of the magnetic moment of the $3/2^-$ state. Unfortunately, this quantity is poorly determined experimentally: $\mu(3/2^-)\approx0.6\mu_N$. The predictions of FPD6 for the E2 moments are rather far from the data: both $3/2^-$ states are calculated to be practically spherical, and the $B(E2)$ transition connecting these states is enhanced by a factor of ~40. Part of this failure comes from too-low a placement of the $f_{5/2}$ level in FPD6, as discussed in detail in Ref. 11, where more examples of KB3G and FPD6 calculations can be found. Therefore, we conclude that the best shell-model estimate of the quadrupole moment of the $3/2^-$ state in $^{57}$Fe is 0.16 eb.

In Ref. 16 it has been pointed out that the ratio of quadrupole moments of the isomeric $^{10}$ state in $^{54}$Fe to the $3/2^-$ state in $^{57}$Fe, $Q([^{54}$Fe$(10^+)]/Q([^{57}$Fe$(3/2^-)])$, represents a stringent constraint. Possible uncertainties in the atomic EFG calculations cancel largely in the experimental determination of the ratio from M"ossbauer data. The most recent value is $Q([^{54}$Fe$(10^+)]/Q([^{57}$Fe$(3/2^-)]) =3.62\pm 0.22$. Unfortunately, the NQM of the isomeric state in $^{54}$Fe is not known experimentally. We have thus calculated the NQM of the isomeric $10^+$ state in $^{54}$Fe in a large-scale shell-model study in which we allowed 8 particles to be promoted from the $f_{7/2}$ orbital to the rest of the shell. We have checked the convergence of our results by performing calculations in which only 6 particles could be promoted; the NQMs were the same at both levels of truncation. For all the interactions used, we find rather similar NQMs: 0.51 eb (KB3F), 0.50 eb (KB3G), and 0.56 eb (FPD6). Using the NQMs of Table I for the isomeric state in $^{57}$Fe, these values correspond to $Q([^{54}$Fe$(10^+)]/Q([^{57}$Fe$(3/2^-)])$ ratios which agree rather well with the measurement for the KB3F and KB3G interactions (2.9 and 3.1, respectively). For the FPD6 interaction, the ratio is significantly too large, as the NQM of the isomer in $^{57}$Fe is severely underestimated. We note that our predicted values for the magnetic moment of the $10^+$ state in $^{54}$Fe (6.4 $\mu_N$ in KB3F,
6.5 \mu_N in KB3G, and 7.1 \mu_N in FDP6) compare well with the experimental value of 7.28 \pm 0.01 \text{n.m.} \text{[18].}

We now turn to our atomic physics studies. The use of the density functional theory for the calculation of EFGs in transition metals is questionable. Recent calculations on CuF showed a deviation of the Cu EFG ranging from +0.50 au for the local density approximation (LDA), and +0.44 au at the generalized gradient approximation (GGA) level (BPW91) to +0.07 au at the hybrid level (B3PW91) \text{[1,21]}, as compared to the experimental value of –0.31(2) au \text{[21]}. In contrast, relativistic ab initio coupled-cluster calculations give –0.34 au \text{[19]}, in perfect agreement with the experimental result.

In this work, we carried out density functional as well as ab initio calculations for the molecules Fe(CO)$_5$ and Fe(C$_5$H$_5$)$_2$. We have adopted a wide range of exchange and correlation functionals for the electronic structure calculations of the free molecules Fe(CO)$_5$ and Fe(C$_5$H$_5$)$_2$ (for the terminology see Refs. \text{[19,22]}): Hartree-Fock-Slater (HFS), X\alpha, Local Density Approximation (LDA), the GGA functionals B-HFS (Slater exchange plus Becke nonlocal exchange), B-LYP (B-HFS plus the correlation functional of Lee, Yang and Parr), B-PW91 (B-HFS plus the correlation functional of Perdew and Wang), the hybrid GGA functionals B3-LYP (Becke three-parameter functional), B3-PW91 (same as B3-LYP except with the nonlocal correlation term of Perdew and Wang), BHH (Becke half-and-half together with the LYP correlation functional), and BHH-LYP (same as BHH but with 0.5 of the Becke nonlocal exchange term added to the energy). For comparison with DFT, we carried out the HF many-body perturbation theory (MBPTn) up to order n=4, as well as coupled-cluster singles doubles including non-iterative triple excitations [CCSD(T)] \text{[23]}. The electronic coupled cluster calculations required three months of CPU time and 20 Gbytes of disk storage on an Origin 2000 SGI. For Fe(CO)$_5$, we investigated solid state effects to the iron electric field gradient by performing HF, B3LYP, and LDA calculations using the program CRYSTAL98 \text{[24]} and the solid state structure given by Böse and Bläser \text{[25]}. Detailed structural data and basis sets used will be published elsewhere \text{[26]}.

The results of our electronic structure calculations for the iron EFGs of Fe(CO)$_5$ and Fe(C$_5$H$_5$)$_2$ are shown in Table \text{[II]}. We first note that the single-reference many-body perturbation theory shows extreme oscillatory behavior and is practically useless for the determination of transition element EFGs. DFT results range from 1.09 au to 1.57 au for Fe(CO)$_5$, and from 1.36 au to 2.49 au for Fe(C$_5$H$_5$)$_2$, depending on the functional applied. If we accept the coupled-cluster result as the most accurate value, the hybrid GGA functionals perform well for Fe(CO)$_5$, while the non-hybrid GGA functionals are preferred for Fe(C$_5$H$_5$)$_2$. We note that for CuCl the BHH functionals gave the best description \text{[13]}. This is clearly not a satisfying situation. On the other hand, an encouraging result is that solid state effects from nearest-neighbor interactions in Fe(CO)$_5$ are small and can basically be neglected. Based on the CCSD(T) EFGs, we obtain from the Mössbauer data of Fe(CO)$_5$ (2.57 mm/sec \text{[24]}) and Fe(C$_5$H$_5$)$_2$ (2.4 mm/sec \text{[25]}) a NQM of 0.177 eb and 0.159 eb, respectively. However, basis set incomplete-ness and relativistic effects may increase the iron EFGs and, therefore, further decrease the NQM \text{[26]}. Consequently, our best estimate using EFGs together with Mössbauer data for these molecules is 0.15(2) eb. In order to improve further on these results, large-scale relativistic coupled-cluster calculations are necessary, which are currently not feasible for such big molecules. We emphasize, however, that EFGs obtained from current DFT for transition element compounds should be taken with some care as the results in Table \text{[II]} show.

In summary, the quadrupole moment of the first 3/2$^{-}$ state in $^{57}$Fe at 14.41 keV, important in Mössbauer spectroscopy, has been calculated using state-of-the-art nuclear and atomic models. Both calculations yield results which are consistent with $Q(3/2^{-})$=0.16 eb, in nice agreement with the recently reported value \text{[2]} and the results of Ref. \text{[29]}. As a by-product of this work, the NQM of the isomeric 10$^{+}$ in $^{54}$Fe has also been calculated. The new value, consistent with the perturbed angular distribution data, is 0.5 eb, i.e., a factor of two greater than the currently recommended value \text{[17]}.

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TABLE I. Results of the shell-model calculations for the quadrupole and magnetic moments of the two lowest 3/2− states in 57Fe using effective interactions KB3F, KB3G, and FPD6. The experimental value of μ(3/2−) is −0.1549(2) μN.

| State | KB3F | KB3G | FPD6 |
|-------|------|------|------|
| 3/2_1 | 0.16 | 0.06 | −0.17 |
| 3/2_2 | −0.16 | −0.07 | 0.17 |

TABLE II. Results of the two-level mixing calculations (mixing amplitudes, quadrupole and magnetic moments, and transition probabilities) for the two lowest 3/2− states in 57Fe using effective interactions KB3F, KB3G, and FPD6. The mixing amplitudes α_1 and α_2 for the 3/2− state have been adjusted to reproduce the experimental value of μ(3/2−) = −0.155 μN (M1) and B(E2) denote 3/2− → 3/2− transition rates. See text for details.

| Method | α_1 | μ(3/2−) | Q(3/2−) | B(M1) | B(E2) |
|--------|-----|---------|---------|-------|-------|
| KB3F   | 0.99 | 0.10    | 0.18    | −0.12 | 0.13  |
| KB3G   | 0.92 | −0.10   | 0.16    | −0.17 | 0.09  |
| FPD6   | 0.87 | 0.14    | 0.02    | −0.02 | 0.10  |

TABLE III. Calculated iron electric field gradient for Fe(CO)5 and Fe(C5H5)2 at various levels of theory. SS denotes solid state calculations. All values are in au.

| Method   | Fe(CO)5 | Fe(C5H5)2 |
|----------|---------|-----------|
| DFT      |         |           |
| Xα       | 1.148   | 1.374     |
| HFS      | 1.092   | 1.363     |
| LDA      | 1.154   | 1.359     |
| SSLDA    | 1.122   | -         |
| BHFS     | 1.187   | 1.434     |
| BLYP     | 1.203   | 1.425     |
| BPW91    | 1.203   | 1.377     |
| B3LYP    | 1.393   | 1.854     |
| SS3B3LYP | 1.357   | -         |
| B3PW91   | 1.395   | 1.806     |
| BHH      | 1.547   | 2.429     |
| BHHLYP   | 1.573   | 2.488     |