Nuclear Quadrupole Moment of ^{57}Fe from Microscopic Nuclear and Atomic Calculations

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The nuclear quadrupole moment (NQM) 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 ^{54}Fe, ^{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$_5$H$_5$)$_2$. Both independent methods yield very similar results. The recommended value is 0.15(2) e b. The NQM of the isomeric 10+ in ^{54}Fe has also been calculated. The new NQM values for ^{54}Fe and ^{57}Fe are consistent with the perturbed angular distribution data.

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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 $+0.44$ e b have been reported [1]. 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 (DFT) for a series of iron-containing solid state compounds. For ^{57}Fe they obtained a NQM of 0.16 e b [2], in contradiction with the previously accepted value of 0.082 e b obtained from Hartree-Fock (HF) EFG calculations [3] and from truncated nuclear shell-model calculations combined with the perturbed angular distribution data [4]. In subsequent work, Su and Coppens obtained a NQM value of 0.12(3) e b using Sternheimer-corrected EFGs [5]. 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. Because of 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 [6]. 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 [7], which were used in Ref. [4] 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 for ^{57}Fe have been performed using the code NATHAN [8]. 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 six 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 ($\sim 2 \times 10^{13}$ nonzero matrix elements) and is one of the largest shell-model diagonalizations performed to date. For all adopted interactions, the results of the truncated and complete calculations are identical. For the lowest 10^+ and 8^+ states in ^{54}Fe we employed the code ANTOINE [9], which is more efficient for high-spin states than NATHAN. Here we allowed a maximum of eight particles to be promoted from the $f_{7/2}$ orbital to the rest of the shell. We have checked the convergence by performing calculations in which only six particles could be promoted; the results, in particular NQMs, were the same at both levels of truncation.

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 interactions KB3F [10] and KB3G [11] are both reasonable attempts to correct the defects of the well-known KB3 interaction [12] in the upper part of the pf shell. As far as ^{54}Fe and ^{57}Fe are 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 $A = 56$ [11]. The FDP6 interaction [13] 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 [14]. 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 $g^s = 0.75 g^s_{\text{bare}}$, $g^l_\pi = 1.1\mu_N$, and $g^l_\nu = -0.1\mu_N$ for $M1$ transitions and moments, e.g., [15]. We adopt the oscillator parameter $b = 1.01A^{1/6}$ fm.

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 a nearly degenerate doublet is quite demanding due to the coupling between these states. In Ref. [16] it has been pointed out, however, that the ratio of quadrupole moments of the isomeric 10^+ state in ^{54}Fe to the $3/2^-$ state in ^{57}Fe, $Q[^{54}\text{Fe}(10^+)]/Q[^{57}\text{Fe}(3/2^-_1)]$ (equal to 3.62 ± 0.22 [17]), represents a stringent constraint, since uncertainties in the atomic EFG calculations cancel in the experimental determination of the ratio from Mössbauer data. Unfortunately, the NQM of the isomeric state in ^{54}Fe is not known experimentally. Therefore, we performed shell-model calculations for this state, which is supposed to be free from complications pertaining to the $3/2^-$ doublet in ^{57}Fe. According to calculations, the isomeric 10^+ state in ^{54}Fe has a rather complex structure, with the three hole configurations representing typically $\approx$50% of the wave function. (We note that in the previous calculations of Ref. [7], only such configurations were allowed.) Although the dominant component of the wave function corresponds to the stretched $(f_{7/2})^7 p_{3/2}$ neutron configuration (46% in KB3F, 41% in KB3G, and 23% in FPD6), other shell-model configurations contribute to the remaining strength. Since FPD6 tends to excite particles to the $f_{5/2}$ orbit rather than the $p_{3/2}$ (FPD6 puts the $f_{5/2}$ orbit too low at $N = 28$), the contribution from the $(f_{7/2})^7 f_{5/2}$ configuration is 19% in FPD6 (it is around 5% for KB3F and KB3G).

In spite of a rather complex structure of the 10^+ state, we find rather similar NQMs for all the interactions used: 0.51 e b (KB3F), 0.50 e b (KB3G), and 0.56 e b (FDP6). [A similar calculation to Ref. [7] gives 0.29 e b (KB3F and KB3G), and 0.23 e b (FPD6).] In addition, our calculations reproduce well the experimental $B(E2; 10^+_1 \rightarrow 8^+_1)$ value of $20.5 \pm 0.5e^2$ fm^4 [18]; it is 28.5, 24.3, and $27.6e^2$ fm^4 for KB3F, KB3G, and FPD6, respectively. (This corresponds to less than 9% deviation from experiment in KB3G for the associated reduced matrix element.) We also 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 $7.28 \pm 0.01\mu_N$ [18]. This comparison with experimental data demonstrates that the effective charges used in our calculations are very reasonable. By taking the experimental $Q[^{54}\text{Fe}(10^+)]/Q[^{57}\text{Fe}(3/2^-_1)]$ ratio and the calculated value of NQM for ^{54}Fe(10^+), we deduce the NQM moment for the isomeric state in ^{57}Fe; it is 0.14(1) e b for KB3G and KB3F, and 0.15(1) e b for FDP6.

Let us now turn to the structure of ^{57}Fe. Our shell-model calculations reproduce well the experimental level scheme of ^{57}Fe. In particular, the low-lying $I^\pi = 3/2^-$ 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 the theoretical predictions.

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 FDP6. Because of too low a placement of the $f_{5/2}$ level in FPD6 (see discussion above), the contributions from higher-lying $3/2^-$ states amount to about 37%.

Because of 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 $3/2^-_1$ state, which has been precisely determined experimentally,

TABLE I. Results of the shell-model calculations for the quadrupole and magnetic moments of the two lowest $3/2^-$ states in ^{57}Fe using effective interactions KB3F, KB3G, and FPD6. The experimental value of $\mu(3/2^-_1)$ is $-0.1549(2)\mu_N$ [19].

		KB3F	KB3G	FPD6
Q	$3/2^-_1$	0.16	0.06	-0.17
(e b)	$3/2^-_2$	-0.16	-0.07	0.17
μ	$3/2^-_1$	-0.32	-0.49	-0.51
(μ_N)	$3/2^-_2$	0.26	0.23	0.49

$\mu(3/2_1^-) = -0.1549(2)\mu_N$. Assuming that the "true" wave functions of the $3/2^-$ doublet are given by a simple rotation of the shell-model states, $|3/2^-\rangle = \alpha_1|3/2_1^-;\mathrm{SM}\rangle + \alpha_2|3/2_2^-;\mathrm{SM}\rangle$, one can determine the mixing amplitudes α_1 and α_2 ($\alpha_1^2 + \alpha_2^2 = 1$) by requesting that the measured value of $\mu(3/2_1^-)$ be reproduced. The results of such two-level mixing calculations are displayed in Table II. 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, $Q(3/2_1^-) \approx 0.17$ e b. The only serious difference is the sign of the magnetic moment of the $3/2_2^-$ state. Unfortunately, this quantity is poorly determined experimentally: $\mu(3/2_2^-) < 0.6\mu_N$. 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 $\sim$40. Part of this failure comes from the placement of the $f_{5/2}$ level in FPD6, as discussed above. (See also 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 $3/2_1^-$ state in ^{57}Fe, based on *both* the $Q[^{54}\mathrm{Fe}(10^+)]/Q[^{57}\mathrm{Fe}(3/2_1^-)]$ ratio analysis and the direct shell-model calculations for ^{57}Fe is 0.15(2) e b.

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 variation of the Cu EFG ranging from +0.50 a.u. for the local density approximation (LDA), and +0.44 a.u. at the generalized gradient approximation (GGA) level (BPW91) to +0.07 a.u. at the hybrid level (B3PW91) [20,21], as compared to the experimental value of −0.31(2) a.u. [22]. In contrast, relativistic *ab initio* coupled-cluster calculations give −0.34 a.u. [20], in perfect agreement with the experimental result.

In this work, we carried out density functional as well as *ab initio* calculations for the molecules $\mathrm{Fe(CO)_5}$ and $\mathrm{Fe(C_5H_5)_2}$. We have adopted a wide range of exchange and correlation functionals for the electronic structure calculations of the free molecules $\mathrm{Fe(CO)_5}$ and $\mathrm{Fe(C_5H_5)_2}$ (for the terminology see Refs. [20,23]): Hartree-Fock-Slater (HFS), Xα, 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 noniterative triple excitations [CCSD(T)] [24]. The electronic coupled-cluster calculations required three months of CPU time and 20 gbytes of disk storage on an Origin 2000 SGI. For $\mathrm{Fe(CO)_5}$ we investigated solid state effects to the iron electric field gradient by performing HF, B3LYP, and LDA calculations using the program CRYSTAL98 [25] and the solid state structure given by Böse and Bläser [26]. Detailed structural data and basis sets used will be published elsewhere [27].

TABLE II. Results of the two-level mixing calculations for the two lowest $3/2^-$ states in ^{57}Fe using effective interactions KB3F, KB3G, and FPD6. The mixing amplitude α_1 for the $3/2_1^-$ state has been adjusted to reproduce the experimental value of $\mu(3/2_1^-) = -0.155\mu_N$. $B(M1)$ and $B(E2)$ denote $3/2_2^- \rightarrow 3/2_1^-$ transition rates. See text for details.

	α_1	$\mu(3/2_2^-)$ (μ_N)	$Q(3/2_1^-)$ (e b)	$Q(3/2_2^-)$ (e b)	$B(M1)$ (μ_N^2)	$B(E2)$ (e^2 fm^4)
KB3F	0.99	0.10	0.18	−0.12	0.13	4
KB3G	0.92	−0.10	0.16	−0.17	0.09	25
FDP6	0.87	0.14	0.02	−0.02	0.10	228
Expt. [19]		<0.6			0.07(1)	5(4)

The results of our electronic structure calculations for the iron EFGs of $\mathrm{Fe(CO)_5}$ and $\mathrm{Fe(C_5H_5)_2}$ are shown in Table III. 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 to 1.57 a.u. for $\mathrm{Fe(CO)_5}$, and from 1.36 to 2.49 a.u. for $\mathrm{Fe(C_5H_5)_2}$, depending on the functional applied. If we accept the coupled-cluster result as the most accurate value,

TABLE III. Calculated iron electric field gradient for $\mathrm{Fe(CO)_5}$ and $\mathrm{Fe(C_5H_5)_2}$ at various levels of theory. SS denotes solid state calculations. All values are in a.u.

Method	$\mathrm{Fe(CO)_5}$	$\mathrm{Fe(C_5H_5)_2}$
	ab initio	
HF	1.394	3.157
SSHF	1.367	⋯
MBPT2	3.511	1.563
MBPT3	−0.740	3.385
MBPT4	9.484	−0.250
CCSD(T)	1.394	1.496
	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
SSB3LYP	1.357	⋯
B3PW91	1.395	1.806
BHH	1.547	2.429
BHHLYP	1.573	2.488

the hybrid GGA functionals perform well for Fe(CO)$_5$, while the nonhybrid GGA functionals are preferred for Fe(C$_5$H$_5$)$_2$. We note that for CuCl the BHH functionals gave the best description [20]. 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 [28]) and Fe(C$_5$H$_5$)$_2$ (2.4 mm/sec [29]) a NQM of 0.177 and 0.159 e b, respectively. However, basis set incompleteness and relativistic effects may increase the iron EFGs and, therefore, further decrease the NQM [27]. Consequently, our best estimate using EFGs together with Mössbauer data for these molecules is 0.15(2) e b. 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 III 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 $Q(3/2_1^-) \approx 0.15(2)$ e b, in nice agreement with the recently reported value [2] and the results of Ref. [30]. 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 e b.

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