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Abstract – The nuclear quadrupole moment (Q) of the $5/2^+$ isomeric state of ^{111}Cd, of particular importance to the interpretation of Perturbed Angular Correlation experiments in condensed matter, was determined by combining existing PAC data with high-level *ab initio* (CCSD(T)) calculations for Cd-dimethyl and hybrid density functional theory for metallic Cd. A revised value of $Q = .641(25)$ b is found, much reduced from earlier estimates. Using the new result together with the values for other Cd isotopes from atomic data, also recently revised, the trend of Q for the $11/2^-$ states in Cd is in perfect agreement with new nuclear covariant density functional theory calculations. Similar theoretical work for metallic Zn and the ZnS molecule, combined with atomic calculations, also results in an equivalent reduction for the reference value of the ^{67}Zn $5/2^-$ ground-state quadrupole moment to $Q = .125(5)$ b.

Motivation. – Precise nuclear quadrupole moments (Q) are essential not only for a detailed understanding of nuclei but also for any quantitative analysis of quadrupole interaction measurements in solids, molecules, or atoms. Normally only the product of Q with the electric-field gradient (EFG, major component V_{zz}) created by the electronic environment, the nuclear quadrupole coupling constant, $\nu_Q = eQV_{zz}/h$, is experimentally available. Thus for determination of reliable values of V_{zz} an accurate number for Q is needed. The EFG, however, is one of a few experimentally available direct measures of the charge distribution in matter. It essentially contains the information on the asymmetry in the local p- (or d-) orbitals, a property intimately related to chemical bonding.

In order to obtain a reliable value for Q, on the other hand, V_{zz} has to be calculated with a highly accurate theoretical method for at least one system where ν_Q is well known. Quantum-mechanical methods have been generally quite successful in the interpretation of atomic and more recently also molecular data [1]. With the advent of density functional (DF) methods a possibility to routinely calculate EFGs in solids became available and for several

test cases the results had been quite promising [2,3]. The present work was initiated as an effort to calculate Q for the $5/2^+$ state in ^{111}Cd, of particular importance for the interpretation of Perturbed Angular Correlation (PAC) measurements in condensed matter. This nucleus represents for PAC what ^{57}Fe is for Mössbauer spectroscopy, by far the most useful. It has found widespread application in solid-state [4], surface [5] and biomolecule [6] studies. Unfortunately, to date only quite uncertain estimates of Q via various methods have been available, ranging from .41 b to 1.32 b (see [7] for history). By using standard DF procedures one had hoped some years ago to arrive at a more reliable value, in particular since the equivalent calculations seemed to reproduce the then accepted Q for the ^{67}Zn ground state [7]. It has been known for some time, however, that the standard DF procedures severely fail to reproduce the known EFG in some cases such as Cu_2O [8], a semiconductor, As and Sb [9], semimetals, and the asymmetry parameter η for the solid halogens [10], insulators. Similarly, values found for Q from DF calculations for halogen [11] or Sb [12] solids were systematically larger than currently accepted ones [13]. During the last

Table 1: Structural data and experimental ν_Q used as input. met = metal; sol = solid; mol = molecule. ** = angle of molecular axis to *ab*-plane; * = Cd-C-H angle.

	a or R1 (Å)	*c* or R2 (Å)	Angle (°)	ν_Q^{exp} (MHz)
Zn^{met}	2.65489[a]	4.85335[a]		12.34(3)[b]
Cd^{met}	2.96313[a]	5.51890[a]		137.2(6)[c]
$\text{Cd(CH}_3)_2^{\text{sol}}$	7.195[d]	4.118[d]	9.33**[d]	946(10)[e]
$\text{Cd(CH}_3)_2^{\text{mol}}$	2.1110[f]	1.0913[f]	110.74*[f]	
ZnS^{mol}	2.0464[g]			9.331(17)[h]

[a]References [14,15], [b]ref. [16], [c]refs. [17,18], [d]ref. [19], [e]ref. [20], [f]present work, [g]ref. [21], [h]ref. [22].

decade a more advanced extension of the standard DF methods, the admixture of some Hartree-Fock (HF) exchange to the DF [23], has been very successfully applied in chemical research. Such hybrid calculations for solids have recently also solved a long-standing problem of standard DF calculations, the failure to reproduce electronic gaps in semiconductors and insulators [24,25]. It has been noted that this procedure significantly changes the computed EFG as well [26]. In the three problematic cases mentioned above a substantial improvement of the agreement of the calculated EFG with the experimental one has recently been achieved [27].

We have therefore now applied the hybrid DF technique in a redetermination of Q for Cd and Zn. By combining the results with new calculations for molecules ($\text{Cd(CH}_3)_2$ and ZnS), atoms ($^3P_1$ state of Zn) and nuclear theory ($11/2^-$ states in Cd isotopes), we have arrived at a consistent picture for Q in both cases, resulting in a substantial shift (more than 15%) from the previously accepted values. This achievement, solving a problem that has been around for some 50 years (see [7] for history), has implications in various connected fields.

Input data. – The structures used for the materials treated are summarized in table 1. They were taken from experimental literature data, for Cd and Zn by extrapolation to $T = 0$. For the cadmium-dimethyl, $\text{Cd(CH}_3)_2$, molecule in the gas phase only partial structural information is available from experiment. Thus for some parameters theoretical values were used as described below.

For comparison with theory one needs to correct the experimental quadrupole coupling constants (table 1) for thermal effects to obtain ν_Q^{cor}. For Cd metal this was found by adding the calculated zero-point vibration EFG change [28]. For Zn this contribution was scaled with the known ratio of the Debye temperatures of Zn and Cd. For (rigid) $\text{Cd(CH}_3)_2$ the determination of ν_Q^{cor} from the experimental solid-state result is described below.

DF calculations for Cd and Zn metal. – All solid state calculations were performed with the full-potential linearized augmented plane waves code WIEN2k [29]. This program package has been known to yield accurate results for band structure and various properties for numerous solids, the precision mainly limited by the

density functional used. In particular it allows for calculation of hyperfine interaction constants at the nucleus, here EFG values, and the contributions of different orbitals. Standard technical parameters (Muffin-tin sphere radius (in atomic units): RMT = $2.3/2.7a_0$ (Zn/Cd); maximum orbital momentum l of wave-function within RMT: $l_{\max} = 10$; maximum K-vector for interstitial wave-function: $K_{\max} = 9/\text{RMT}$; maximum G-vector in charge density Fourier expansion: $G_{\max} = 12a_0^{-1}$) were used. The calculations were made in the scalar relativistic approximation, with an additional local d-orbital in order to increase basis set flexibility, and included the semi-core p-states for zinc and cadmium. Calculations with spin-orbit interaction, presently only possible using standard functionals, were performed in order to account for this (very small) contribution to the EFG. In the case of the hexagonal close-packed metals Cd and Zn a complication arises due to their complex band structure. This requires in principle an extremely dense mesh of k-points, not possible in practical calculations. A solution to this problem was found by extrapolation of the dominant p- and d-contributions to infinite number of k-points, using $1/k_z^2$ as coordinate. It is demonstrated in fig. 1s[1] for conventional DF calculations for Cd, using a generalized gradient approximation (PBE) [30]. Very similar results are obtained for Zn (see also [27]). Calculations with other standard functionals have shown that the results for the EFGs, of primary concern in the present work, only change to a very minor extent, typically 1%, with different choices. They have been used to obtain an idea about the theoretical errors, however.

A recent extension of the WIEN2k code allows to use hybrid functionals also for solids. In hybrid DF methods the exchange part of the "standard" functional is replaced by a fraction α with the exact exchange obtained in a Hartree-Fock procedure. The present calculations with such a hybrid functional used this method with unscreened HF exchange as described in [26]. These calculations require about three orders of magnitude longer running times than the standard ones, however. Therefore extensive tests of the necessary input conditions were performed. We have now applied this procedure to Zn and Cd

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[1]See Supplementary Material `CdZnSuMa.doc` for tables 1s–3s and figs. 1s and 2s.

Table 2: V_{zz} values (10^{21} V/m^2) from hybrid DF calculations.

	Zn$^{\mathrm{met}}$	Cd$^{\mathrm{met}}$	Cd(CH$_3$)$_2^{\mathrm{mol}}$
V_{zz}_PBE	+3.400	+7.360	−56.53
V_{zz}^p_PBE	+4.561	+8.804	−63.81
V_{zz}^d_PBE	−1.120	−1.305	+6.32
δ^p (%)	+19.2	+22.4	+9.4
V_{zz}_HYB	+4.268	+9.301	−62.44

Table 3: V_{zz} (10^{21} V/m^2) for the Cd(CH$_3$)$_2$ molecule computed with various quantum chemistry methods.

Method	V_{zz}
HF	−76.0
MP2	−63.6
PBE	−55.0
PBE0	−61.3
BHandH	−66.8
CCSD(T)	−64.6

metal, using for simplicity the conventional mixing parameter $\alpha = 0.25$ [31,32] and neglecting the semi-core states for efficiency reasons. Similar to [27] it was found that this increases the (dominant) p-contribution to the EFG by a factor of $1 + \delta^p$, largely independent of the k-point mesh, while the d-contribution stays almost unchanged. Since the EFG results are somewhat sensitive to the number of unfilled states included in the HF program, calculations to a large cut-off energy (up to 3 Ry above the Fermi level) had to be made as demonstrated in fig. 2s (see footnote [1]) for Cd and Zn. The results obtained are $\delta^p = 18.1\%$ for Cd and 17.3% for Zn. A few, more expensive, hybrid DF calculations with inclusion of the semi-core states were also made. It was found that this further increases the δ^p values by factors of 1.24 (Cd) and 1.11 (Zn). The net result of this procedure is an increase of the theoretical V_{zz} values, dependent, of course, on the mixing parameter α chosen. Final results are included in table 2.

Molecular calculations for cadmium-dimethyl, Cd(CH$_3$)$_2$. – The accuracy attainable for the EFG in free molecules by *ab initio* quantum-chemical methods has in recent years led to quite precise values of Q in many cases [1]. We have therefore used such methods for the Cd(CH$_3$)$_2$ molecule, where data of ν_Q, in the solid state, however, are available [20]. All calculations were performed with the DIRAC program package [33] at the full 4-component relativistic level. Initially the experimentally determined gas phase structure for the molecule [34] (in the eclipsed configuration) was used, containing some "guessed" parameters, for the distance R(C-H) = 1.09 Å and for the angle Cd-C-H = 110.521°. Then the basis set convergence of the EFG results was explored using the PBE0 functional [31] (see table 1s (see footnote [1])) and a combination of the fully uncontracted relativistic basis sets $(c)vxz(x = 2, 3, 4)$ by Dyall [35] for Cd and the correlation consistent basis sets $cc\text{-}p(C)VXZ$ $(X = D, T, Q)$ by Dunning [36,37] in their completely uncontracted form for C and H. From this study it was concluded that the combination of the fully uncontracted $cv3z$ basis set for Cd and the fully uncontracted $cc\text{-}pCVTZ$ basis sets for C and H ($cv3z/cc\text{-}pCVTZ$) is sufficient. An optimization of the molecular structure yielded only minor changes (see table 1). The Cd-C distance, 2.111 Å, was found in perfect agreement with the experimental result, 2.112(4) Å. The actual geometry of the CH$_3$ units, not

known from experiment, turned out to be of minor importance for the EFG calculation. In particular an eclipsed or staggered configuration of the hydrogen atoms gave essentially the same V_{zz} at Cd. Extensive calculations for different geometries showed a rather strong dependence on the Cd-C distance, however, with essentially no effect of the C-Cd-C bond angle (see table 2s (see footnote [1])), in agreement with earlier results for Hg molecules [38,39]. Finally a fully relativistic calculation at the level of the coupled cluster singles and doubles theory with perturbative triples corrections, CCSD(T) [40] was performed in the same way as previously for Hg(CH$_3$)$_2$ [38], leading to the molecular EFG adopted. Results for V_{zz} using various methods are included in table 3 for comparison, demonstrating that the PBE0 functional performs reasonably well, underestimating V_{zz} by $3.3 \cdot 10^{21}$ V/m^2 or $\sim 5\%$, as compared to the CCSD(T) bench mark value. Interestingly, using the PBE functional the calculated V_{zz} is much lower than the CCSD(T) result (by $\sim 15\%$), corroborating the discussion of inadequacies of this functional in the section on DF calculations for the metals above.

Solid-state calculations for Cd(CH$_3$)$_2$. – These calculations served the purpose to determine the necessary corrections due to solid-state effects on the measured ν_Q. The solid-state effect on the EFG could in principle come from two sources, the direct intermolecular interactions in the solid and the change of the molecular structure, mainly the Cd-C distance, caused by these. Both contributions have been estimated by a DF calculation of the solid using the local density approximation (LDA) [41]. The choice of LDA was made because out of the simple DFs it best reproduces the Cd-C distance for the free molecule, giving 2.1185 Å. The known lattice constants of the high-temperature tetragonal phase and the angle formed by the molecular axis with the ab-plane [19] (see table 1) were adopted. The CH$_3$ geometry was kept fixed, with the Cd-C distance and the intermolecular separation varied. It turned out that both effects lead to a reduction of the EFG, 5.4% and 5.1%, respectively. Detailed results are given in table 3s (see footnote [1]). The theoretical lengthening of the Cd-C distance by 0.04 Å in the solid is larger than for the experimental, rather imprecise data, 2.112(4) Å [34] to 2.132(3) Å [19]. Such an overestimation (typically a factor of 2) of the intermolecular

Table 4: Final V_{zz} (10^{21} V/m^2), ν_Q^{cor} (MHz) and Q (b).

	Zn$^{\text{met}}$	ZnS$^{\text{mol}}$	Zn$^{\text{at}}$	Cd$^{\text{met}}$	Cd(CH$_3$)$_2$
V_{zz}	+4.268	+3.50	−6.23	+9.287	−64.62
ν_Q^{cor}	+12.64	(+)9.331	−18.782	+139.4	(−)1002
Q	0.122(5)	0.110(10)	0.125(5)	0.621(25)	0.641(25)

interaction effect is generally found with the standard DF procedures [10]. The calculated EFG shift was therefore reduced by a factor of 0.5. In addition one expects thermal motion contributions. From the calculations for bent molecules (see above) one finds, surprisingly, that the intramolecular bending motion will have negligible effect, not to be expected *a priori*. The zero-point librational motion effect is hard to estimate, since no solid-state vibrational frequencies are available from experiment. In analogy to solid bromine [10], with similar melting point and moment of inertia, one can estimate an additional 0.4% reduction in the EFG. This adds up to a total effect of 5.6%, with a significant uncertainty, however.

The same solid-state hybrid procedure used for the metals was also applied to an (effectively) isolated Cd(CH$_3$)$_2$ molecule in a rhombohedral cage of $16 \times 16 \times 20 a_0^3$. In agreement with the quantum chemistry calculations (see above) the result for the EFG (table 2) is only somewhat smaller than the CCSD(T) value.

Molecular calculations for ZnS. − For determining Q of the ^{67}Zn 5/2$^-$ ground state from molecular calculations, the only case available where geometry [21] and ν_Q [22] are known with precision is ZnS. Thus in principle it seemed quite straightforward to get a precise value of Q. The EFG was calculated to CCSD(T) accuracy with the MOLCAS [42] code. Relativistic effects were accounted for at scalar relativistic approximation. We used a standard procedure which is in detail described in the review paper [43] and references therein. Unfortunately the value (table 4) is quite small for this molecule, especially due to the fact that nuclear and electronic contribution partly cancel each other. The series of electronic EFG values indicates that the fully contracted basis set on the CCSD(T) level is well saturated. Correlating 34 electrons is also adequate as increasing the number to 42 does not change the result. Some effects may, however, be expected from higher excitations as full iterative triples and quadruples. We do not expect that the total error in the electronic contribution to the EFG exceeds $0.3 \cdot 10^{21}$ V/m^2.

EFG for atomic $^3P_1$ states. − In two classical papers [44,45] (in 1969!) V_{zz} for the $^3P_1$ state in Zn and Cd has been estimated using the r^{-3} expectation value extracted from the observed magnetic hyperfine interaction. For almost 50 years these have been used as reference to find Q for these elements. For the recent laser experiments of Cd isotopes in an ionic state [46] V_{zz} has been recalculated with the multi-configuration Dirac-Hartree-Fock [47]

approach and found to be about 14% higher than the old result would suggest. More recent experimental and theoretical work for the $^3P_2$ state of the Cd isotopes [48] has completely confirmed this finding. For the case of ^{67}Zn there is also some evidence that the old reference value could be wrong. Recent multi-configuration Dirac-Fock calculations [49] have failed to reproduce the B-factor for the $^3P_1$ state, the quadrupole coupling constant, measured precisely a long time ago [50], while perfect agreement was found for the A-factor, the magnetic hyperfine coupling constant. For normalization the authors have employed the earlier value, $Q(^{67\text{g}}$ Zn 5/2$^-$) = .150 b [51]. In table 4 we have extracted V_{zz} from this work and recalculated Q. The increase of the EFG relative to the classical result by 20.3% is similar to the finding for Cd (13.8%), and such an effect can also be seen when comparing the modern calculation of Q for ^{201}Hg [52] with the classical method [53,54].

Error discussion. − In order to estimate the expected accuracy of the nuclear quadrupole moments determined, a careful evaluation of possible errors is needed. The precision of the experimental ν_Q value, estimation of the zero-point vibration correction (and solid-gas effect) and the accuracy of the structure used are influencing all cases. For the hybrid DF calculations the difference due to choice of density functional, ambiguity due to choice of α, and error due to cut-off energy in HF must be considered as well. The (absolute) accuracy of the CCSD(T) procedure, estimated to 1.5%, is primarily limited by the incompleteness of the basis function space. Following [46] we have assumed for the atomic calculations a 4% error. In table 4 the resulting estimated errors of Q are included for all cases considered. As final values we adopt:

$Q(^{111\text{m}}$Cd 5/2$^+$) = .641(25) b and $Q(^{67\text{g}}$Zn 5/2$^-$) = .125(5) b. Even when only the DF calculations for the metals are considered, a renormalization of Q for Cd automatically requires one for Zn as well, since the calculated ratio of V_{zz} in Zn to the one in Cd is essentially independent of the DF used or the HF mixing parameter.

Nuclear theory calculations. − The nuclear moments for high-spin states often show a remarkable simplicity as function of neutron number. A particular example are the quadrupole moment values of the 11/2$^-$ states in Cd isotopes. They have long been known to change very systematically, and their linear trend had actually been used in early estimations of Q for the ^{111}Cd 5/2$^+$ state [55,56]. Such a linear trend has recently been confirmed with high-precision collinear laser
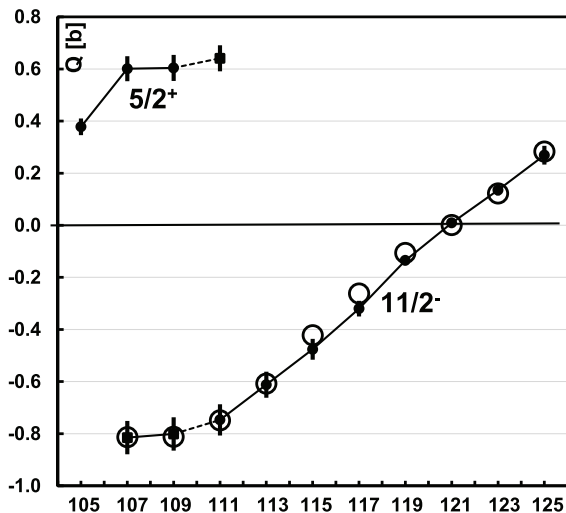
Fig. 1: New quadrupole moment values for $11/2^-$ and $5/2^+$ states in light Cd isotopes from atomic (dots) and solid state (squares) data, for $11/2^-$ states compared to nuclear theory (open circles); for better visibility the experimental errors are shown increased by a factor of 2.

spectroscopy [46], and then was explained within nuclear covariant density functional theory (CDFT) [57]. Since the early perturbed angular distribution (PAD) experiments [56] relate the quadrupole moments of the short-lived $11/2^-$ states in ^{107,109}Cd to that of ^{111}Cd $5/2^+$, determined here with high precision, we can now further extend the observed trend. In fig. 1 a saturation of the quadrupole moments is clearly demonstrated for ^{107,109}Cd. This saturation is fully consistent with the prediction from our new nuclear calculations with the same CDFT procedure used earlier for the heavier isotopes. The agreement with the experimental results, obvious there, is very satisfactory. Actually, one might use the theoretical nuclear theory ratio of $Q(11/2^-)$ for ^{109}Cd to ^{111}Cd, combined with the Q ratio of ^{111}Cd $5/2^+$ to ^{109}Cd $11/2^-$ from the PAD experiments, in order to arrive at a completely independent "nuclear theory" value for Q of ^{111}Cd $5/2^+$ as .636 (45) b, fully consistent with the results in table 4. Confidence in such a procedure comes from the fact that the theoretical $Q(11/2^-)$ ratios for ^{111}Cd/^{113}Cd and ^{107}Cd/^{109}Cd agree extremely well with the experimental ones, known with high precision. In estimating the error of this approach we have added the error of the atomic result for V_{zz} to the one of nuclear theory as evident from fig. 1.

Conclusions and outlook. – Calculations of the nuclear quadrupole moment for $Q(^{111m}$Cd $5/2^+)$ are presented based on independent atomic, molecular, solid-state and nuclear approaches, all converging to a significant reduction of the currently accepted literature number. We obtain as new value 0.641(25) b. Similarly a new result for $Q(^{67g}$Zn $5/2^-) = .125(5)$ b is found.

The present results shed doubt on the accuracy of DF calculation of EFGs in solids when non-hybrid functionals

are applied and no high-level *ab initio* (such as CCSD(T)) calculation is presented to validate the approach. An example is the recent value for Q for ^{111}Cd $5/2^+$ calculated with standard DF methods [58], where a careful estimate of the error on Q was presented, and only the quality of the functional was inadequate. In fact applying the reduction of V_{zz} by $\sim 15\%$ indicated by the data in table 2 (from the PBE functional to the CCSD(T) result) the value of Q presented in [58] is in excellent agreement with the value presented here. Obviously the influence of the partial inclusion of HF exchange would have to be studied for each solid, and (presumably) would improve the results. Preliminary calculations indicate that the effect is markedly different in every case, however.

As far as the nuclear physics output of the present work is concerned, the explanation of the experimental trend of Q for the $11/2^-$ states by CDFT is certainly gratifying. The emerging trend for the $5/2^+$ states, hopefully soon augmented by new laser spectroscopy (^{101,103,105}Cd) and PAC (^{113,115}Cd) data, will require a more microscopic nuclear theory approach, however. How could one then further test the reliability of the present results? Obviously a new calculation for the $^3P_1$ state of Zn with another atomic code (or results for another atomic state) would be decisive. Also further microwave experiments for simple Zn containing molecules should be helpful. For the ^{111}Cd $5/2^+$ state the chances to obtain a still more precise value for Q are not obvious. Only a PAC measurement in a free molecule could solve this problem. Unfortunately, early attempts of such experiments in the 1970s have failed. Perhaps these courageous efforts could be more successful using modern techniques of isotope production.

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