Magnetic-Field-Induced Quadrupole Splitting in Gaseous and Liquid ^{131}Xe NMR: Quadratic and Quartic Field Dependence

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A theory for the magnetic-field-dependent quadrupole splitting in the ^{131}Xe NMR spectra in isotropic media is presented and tested by *ab initio* electronic structure calculations. Evidence exists only for even-power magnetic field dependence. The dominant mechanism is verified to be the electric field gradient caused by the diamagnetic distortion of the atomic electron cloud, quadratic in the magnetic field. The computed results are in excellent agreement with the recent experiment by Meersmann and Haake.

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Nonvanishing average electric field gradient (EFG) at the site of an atomic nucleus possessing electric quadrupole moment leads to splittings in the nuclear magnetic resonance (NMR) spectra [1,2]. In cubic or higher nuclear site symmetries, as for the spherical symmetry of a free atom, such splittings are absent. Meersmann and Haake [3] recently measured quadrupole splittings in the spectra of ^{131}Xe in gas and isotropic [4] liquid phases as a function of the applied magnetic field, B. In addition to the earlier observed B-independent splitting [5] caused by EFGs at the inner surface of the (nonspherical) sample container, a splitting of a few Hz, increasing with B, was detected at $7.05 \leq B \leq 16.92$ T [3]. A separation of the surface effect from the field-induced splitting in the bulk of the medium was attempted by using three kinds of samples with different surface interaction: a gas-phase sample in a tube filled with capillaries, a gas-phase sample in a plain tube, and a liquid-phase sample; see Fig. 1.

A qualitative explanation in terms of a B-induced diamagnetic deformation of the electron cloud of the Xe atom was proposed by Salsbury and Harris [7], who suggested both linear and quadratic B dependence. Because of the properties of the nuclear electric quadrupole moment tensor [8], the quadrupole interaction terms in the NMR Hamiltonian, $H_{K,Q}^{\mathrm{NMR}} = \mathbf{I}_K \cdot \boldsymbol{\mathcal{B}}_K \cdot \mathbf{I}_K$, are bilinear in the nuclear spin operator, $\mathbf{I}_K$, of nucleus K. The requirement of time-reversal invariance forbids the existence of energy terms bilinear in $\mathbf{I}$ and exhibiting odd powers in B, for closed-shell systems, like the Xe atom [9,10]. For odd-power magnetic field dependence, at least *trilinear* dependence on $\mathbf{I}$ must be considered, such as in the term linear in B proposed in Ref. [7]. To the authors' knowledge, such terms in H_{NMR} have so far eluded observation in any system [11]. If one accepts the possibility of residual constant (surface) contributions in all of the three experimental data sets of Ref. [3], no linear term in B is necessary here either: all three can be fitted with a coefficient of the quadratic term equal to 14 mHz/T^2 [6].

Concentrating on the energy terms bilinear in $\mathbf{I}$ and exhibiting even-power B dependence, Ref. [7] was able to give only a qualitative scaling argument in support of the validity of their suggestion. The purpose of the present Letter is to identify the physical mechanisms contributing to the second and fourth power B dependence of quadrupole coupling in atomic closed-shell systems. We report explicit *ab initio* electronic structure calculations using analytical linear and nonlinear response theory [12] for the effect in ^{131}Xe. The suggested [7] diamagnetic mechanism, quadratic in B, is verified to be dominant by quantitative agreement with the experiment.

In a closed-shell system, the Cartesian $\epsilon\tau$ component of the quadrupole coupling tensor $\mathcal{B}_{\epsilon\tau}$ can be written as the first derivative of the Taylor series expansion of the energy with respect to the bilinear product of nuclear spin

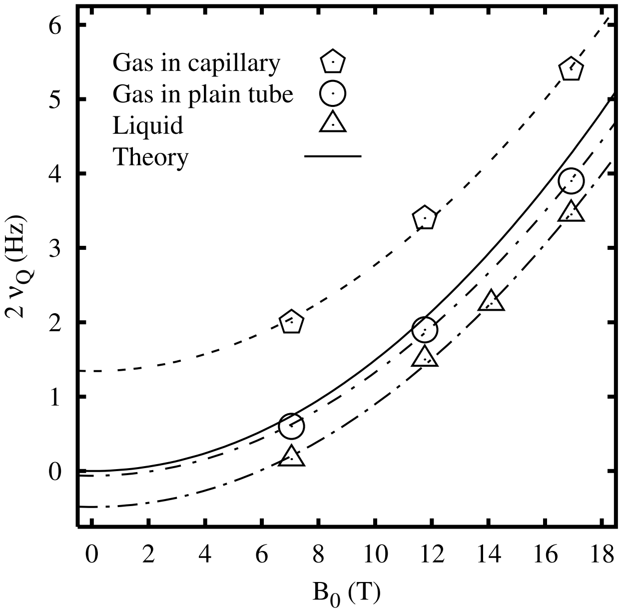

FIG. 1. Experimental [3] and theoretical (RAS-III + mvd, present work) ^{131}Xe NMR quadrupole splitting as a function of magnetic field. Results of least-squares fits (dashed lines) [6] to the experimental data are also shown.

components [13]

$$\mathcal{B}_{\epsilon\tau} = \frac{1}{2\pi}\frac{dE}{dI_\epsilon I_\tau} = \frac{1}{2\pi}\left(\frac{\partial E}{\partial I_\epsilon I_\tau}\right)_0 + \frac{1}{2\pi}\frac{1}{2}\left(\frac{\partial^3 E}{\partial I_\epsilon I_\tau \partial B^2}\right)_0 B^2 + \frac{1}{2\pi}\frac{1}{24}\left(\frac{\partial^5 E}{\partial I_\epsilon I_\tau \partial B^4}\right)_0 B^4 + \ldots$$

$$\equiv \mathcal{B}^{(0)}_{\epsilon\tau} + \frac{1}{2}\mathcal{B}^{(2)}_{\epsilon\tau}B^2 + \frac{1}{24}\mathcal{B}^{(4)}_{\epsilon\tau}B^4 + \ldots . \qquad (1)$$

Here $\mathbf{B} = B\hat{\mathbf{z}}$, and the subscript 0 denotes derivatives taken at vanishing perturbations. No terms with odd powers in B occur. The first term corresponds to the absence of B and arises in general either from true quadrupole coupling $\mathcal{B}^{q(0)}$ [1,14] or from pseudoquadrupole coupling $\mathcal{B}^{pq(0)}$ where magnetic hyperfine interactions produce energy terms bilinear in $\mathbf{I}$ [15]. For spherical symmetry, $\mathcal{B}^{(0)}_{\epsilon\tau} = 0$.

For large nuclear Zeeman interaction as compared to quadrupole coupling, $H_Q^{\mathrm{NMR}} \approx \frac{3}{2}\mathcal{B}_{zz}I_z^2 = \Delta\mathcal{B}I_z^2$ where $\Delta\mathcal{B} = \mathcal{B}_{zz} - \mathcal{B}_\perp$ is the anisotropy of $\mathcal{B}$ with respect to the direction of $\mathbf{B}$. For $I = 3/2$ nuclei such as ^{131}Xe, this leads to a symmetric triplet spectrum with the line splitting $\nu_Q = 3|\mathcal{B}_{zz}|$, hence the distance between the two outmost lines is, to fourth order in B,

$$2\nu_Q = 4\Delta\mathcal{B} \approx 2\Delta\mathcal{B}^{(2)}B^2 + \frac{1}{6}\Delta\mathcal{B}^{(4)}B^4. \qquad (2)$$

Consideration of the Breit-Pauli molecular Hamiltonian [16] leads to the following leading true quadrupole [superscript q, contributions of $\mathcal{O}(\alpha^0)$, with α the fine structure constant] and pseudoquadrupole [pq, $\mathcal{O}(\alpha^4)$] contributions to quadratic and quartic quadrupole couplings

$$\Delta\mathcal{B}^{(2)} = \Delta\mathcal{B}^{q(2)} + \sum_{n=1}^{4}\Delta\mathcal{B}^{pq,n(2)}; \qquad \Delta\mathcal{B}^{(4)} = \Delta\mathcal{B}^{q(4)} + \sum_{n=1}^{2}\Delta\mathcal{B}^{pq,n(4)}, \qquad (3)$$

where the individual terms are

$$\begin{aligned}
\mathcal{B}^{q(2)}_{\epsilon\epsilon} &= \frac{1}{\pi}\langle\langle h^{\mathrm{efg}}_{\epsilon\epsilon}; h^{\mathrm{susc}}\rangle\rangle_0; & \mathcal{B}^{q(4)}_{\epsilon\epsilon} &= \frac{6}{\pi}\langle\langle h^{\mathrm{efg}}_{\epsilon\epsilon}; h^{\mathrm{susc}}, h^{\mathrm{susc}}\rangle\rangle_{0,0}\,, \\
\mathcal{B}^{pq,1(2)}_{\epsilon\epsilon} &= \frac{1}{2\pi}\langle\langle h^{\sigma^d}_{\epsilon}; h^{\sigma^d}_{\epsilon}\rangle\rangle_0; & \mathcal{B}^{pq,1(4)}_{\epsilon\epsilon} &= \frac{6}{\pi}\langle\langle h^{\sigma^d}_{\epsilon}; h^{\sigma^d}_{\epsilon}, h^{\mathrm{susc}}\rangle\rangle_{0,0}\,, \\
\mathcal{B}^{pq,2(2)}_{\epsilon\epsilon} &= \frac{1}{2\pi}\langle\langle h^{\mathrm{pso}}_{\epsilon}; h^{\mathrm{pso}}_{\epsilon}, h^{\mathrm{susc}}\rangle\rangle_{0,0}; & \mathcal{B}^{pq,2(4)}_{\epsilon\epsilon} &= \frac{3}{\pi}\langle\langle h^{\mathrm{pso}}_{\epsilon}; h^{\mathrm{pso}}_{\epsilon}, h^{\mathrm{susc}}, h^{\mathrm{susc}}\rangle\rangle_{0,0,0}\,, \\
\mathcal{B}^{pq,3(2)}_{\epsilon\epsilon} &= \frac{1}{\pi}\langle\langle h^{\mathrm{fc}}_{\epsilon}; h^{\mathrm{sd},\epsilon}_{\epsilon}, h^{\mathrm{susc}}\rangle\rangle_{0,0}; & \mathcal{B}^{pq,4(2)}_{\epsilon\epsilon} &= \frac{1}{2\pi}\sum_{\nu}\langle\langle h^{\mathrm{sd},\nu}_{\epsilon}; h^{\mathrm{sd},\nu}_{\epsilon}, h^{\mathrm{susc}}\rangle\rangle_{0,0}\,.
\end{aligned} \qquad (4)$$

The most important perturbation operators involved in Eq. (4) are

$$\begin{aligned}
H^{\mathrm{efg}} &\equiv \sum_{\epsilon\tau} h^{\mathrm{efg}}_{\epsilon\tau} I_\epsilon I_\tau = -\frac{1}{2}\frac{Q}{I(2I-1)}\sum_{\epsilon\tau} I_\epsilon \sum_i \frac{3r_{iK,\epsilon}r_{iK,\tau} - \delta_{\epsilon\tau}r_{iK}^2}{r_{iK}^5} I_\tau\,, \\
H^{\mathrm{susc}} &\equiv h^{\mathrm{susc}}B^2 = \frac{1}{8}\sum_i (r_{iO}^2 - r_{iO,z}^2)B^2,
\end{aligned} \qquad (5)$$

the EFG and diamagnetic susceptibility (with gauge origin at O) operators, respectively. The standard hyperfine operators for diamagnetic nuclear shielding, $h^{\sigma^d}_\epsilon$, paramagnetic nuclear spin-electron orbit, $h^{\mathrm{pso}}_\epsilon$, Fermi contact, h^{fc}_ϵ, and spin-dipole interactions, $h^{\mathrm{sd},\nu}_\epsilon$, appear in Eq. (4) [16,17]. Two quartic terms, analogous to $\mathcal{B}^{pq,3(2)}_{\epsilon\epsilon}$ and $\mathcal{B}^{pq,4(2)}_{\epsilon\epsilon}$ but including an additional h^{susc}, have been omitted from Eqs. (3) and (4) due to software limitations. In the light of the overall importance of the pq terms (see below), this omission is insignificant. The effect of H^{susc} on an atom can be described as elongation in the direction of $\mathbf{B}$. In the molecular case, there are additional contributions involving the orbital Zeeman interaction [18].

Equation (4) is expressed in terms of linear, quadratic, and cubic response functions ($\langle\langle A;B\rangle\rangle_0$, $\langle\langle A;B,C\rangle\rangle_{0,0}$, and $\langle\langle A;B,C,D\rangle\rangle_{0,0,0}$, respectively) corresponding to time-independent perturbations A to D [12]. These response functions correspond to second-, third-, and fourth-order Rayleigh-Schrödinger perturbation theory expressions, respectively, involving the same operators.

Ab initio self-consistent field (SCF) and multiconfiguration SCF (MCSCF) response theory [12] calculations of all the terms in Eq. (4) were carried out for the Xe atom using the DALTON software [19]. The necessary analytical singlet linear, singlet quadratic, triplet quadratic, and singlet cubic response functions were implemented in Refs. [20–23], respectively. The details of the wave functions can be found in Table I. The SCF basis set convergence of the results has been monitored [18] and a saturated basis has

TABLE I. Numerical results for the magnetic-field-induced ^{131}Xe NMR quadrupole splitting: The coefficients $2\Delta\mathcal{B}^{(2)} = 2\nu_Q^{(2)}/B^2$ and $1/6\Delta\mathcal{B}^{(4)} = 2\nu_Q^{(4)}/B^4$ of the quadratic and quartic terms, respectively, are given.[a]

	$2\Delta\mathcal{B}^{(2)}$ (mHz/T^2)				$1/6\Delta\mathcal{B}^{(4)}$ (pHz/T^4)			
Theory	q	q + PS[b]	q(mvd)[c]	q + q(mvd)	q	q + PS[b]	q(mvd)[d]	q + q(mvd)
SCF	11.879	14.163	2.9398	14.819	−0.722 65	−0.861 57	−0.184 02	−0.906 66
RAS-I[e]	11.318	13.494	2.8385	14.156	−0.623 42	−0.743 27	−0.158 00	−0.781 42
CAS[f]	11.282	13.451	2.8379	14.120	−0.617 01	−0.735 63	−0.157 34	−0.774 36
RAS-II[g]	12.179	14.520	2.9754	15.155	−0.731 98	−0.872 70	−0.184 95	−0.916 94
RAS-III[h]	11.915	14.206	2.9261	14.842	−0.699 95	−0.834 51	−0.175 96	−0.875 91
Expt.[i]				±14				⋯

[a] The true quadrupole interaction terms q discussed in the text. An uncontracted spherical Gaussian $(25s21p20d7f)$ basis set, based on Ref. [24] and supplemented with both large- and small-exponent functions, was used. Details will be presented in a later publication [18].

[b] Supplemented with *a posteriori* multiplicative relativistic correction of the Xe $5p$ EFG integrals $[C_{\rm QR}(\rm DF) = 1.192\,24]$ of Pyykkö and Seth (PS), Ref. [25].

[c] The first-order relativistic mass-velocity and one-electron Darwin interaction [16] corrections [of $\mathcal{O}(\alpha^2)$] to the true quadrupole contribution calculated as $\mathcal{B}^{q(2)}_{\epsilon\epsilon}(\text{mvd}) = 1/\pi\langle\langle h^{\rm efg}_{\epsilon\epsilon}; h^{\rm susc}, h^{\rm mv} + h^{\rm Dar}\rangle\rangle_{0,0}$. The $\mathcal{O}(\alpha^4)$ spin-orbit contribution would be of second order in $h^{\rm so}$ and require triplet cubic response theory. It is expected to be small as compared to the mvd terms.

[d] As footnote c but $\mathcal{B}^{q(4)}_{\epsilon\epsilon}(\text{mvd}) = 6/\pi\langle\langle h^{\rm efg}_{\epsilon\epsilon}; h^{\rm susc}, h^{\rm susc}, h^{\rm mv} + h^{\rm Dar}\rangle\rangle_{0,0,0}$.

[e] A single-reference restricted active space MCSCF [26] wave function correlating 8 electrons by single and double excitations from the occupied valence $5s5p$ orbitals into the $5d$ orbitals. A total of 87 Slater determinants.

[f] A complete active space MCSCF [27] wave function corresponding to a full CI expansion in the $5s5p5d$ atomic orbital space and correlating 8 electrons. A total of 2016 Slater determinants.

[g] Single-reference wave function correlating 18 electrons by singles and doubles $4d5s5p \rightarrow 5d4f6s6p6d$. A total of 6532 Slater determinants.

[h] Single-reference wave function correlating 26 electrons by singles and doubles $4s4p4d5s5p \rightarrow 5d4f6s6p6d5f7s7p$. A total of 32 165 Slater determinants.

[i] Reference [3].

been used in the results quoted in Table I. The true quadrupole contribution q is slightly smaller than the experimental coefficient of the quadratic splitting, and completely dominating as compared to the pseudoquadrupole terms pq. Using the RAS-II wave function, the quadratic splittings $2\Delta\mathcal{B}^{(2)}$ of −9.5, 22 000, 7900, and 3000 pHz/T^2 are found for the first to fourth pq terms, respectively, to be compared with q that is about 5 orders of magnitude larger. Electron correlation has only a minor effect. After the substantial relativistic correction, obtained either semiempirically [25] or as first-order perturbation (mvd), the final theoretical value of 14.1–14.9 mHz/T^2 is arrived at. We do not know the experimental error limits, but already taking into account the 5% uncertainty in the $Q_{^{131}\rm Xe} = -0.117(6) \times 10^{-28}$ m^2 [28] used in the calculations yields a perfect agreement with the experimental coefficient 14 mHz/T^2.

Results for the quartic splitting, for which there is no experimental datum, are also shown in Table I. The dominance of q terms over pq is clear here as well: RAS-II gives $pq, 1 = 9.8 \times 10^{-6}$ aHz/T^4 and $pq, 2 = 0.30$ aHz/T^4, at least 7 orders of magnitude smaller than q. The quartic contributions are more sensitive to basis set and correlation than the quadratic ones. Reliable order-of-magnitude estimates can be made, though. The magnitude of the total quartic splitting would be around 1 mHz in a field of 100 T. For present experiments, it is thus enough to consider the quadratic term.

To summarize, we have identified the physical mechanisms, due to both true quadrupole and pseudoquadrupole interactions, of the magnetic field-dependent quadrupole splitting in the NMR spectra of closed-shell atoms, and carried out *ab initio* calculations on Xe to evaluate the different terms. The dominant effect is found to be the interaction of the nuclear quadrupole moment with EFG created by the diamagnetic distortion of the electron cloud, quadratic in B. The pseudoquadrupole as well as all terms quartic in B are found to be negligibly small. After consideration of scalar relativistic effects, a quantitative agreement with experiment is reached for ^{131}Xe.

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[9] Upon time reversal, $t \rightarrow -t$, the electron spin $s_i \rightarrow -s_i$, $I \rightarrow -I$, and $B \rightarrow -B$, but for energies $E \rightarrow E$. Hence, for a closed shell electronic system an allowed energy term can only be proportional to $I^2 B^{2n}, n = 0, 1, 2, \ldots$.

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