Electric field gradient at ^7Li site in LiD.

Polarization of core orbitals and computation of nuclear quadrupole coupling constants using Gaussian basis sets

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ABSTRACT: Most standard Gaussian basis sets for first row atoms, even large sets designed to converge on a ‘complete basis set’ limit, systematically overestimate the electric field gradient at nuclear sites for first row atoms, resulting in errors of up to 15% in the computation of nuclear quadrupole coupling constants. This error results from a failure to include tight d functions, which permit the core 1s orbitals to distort under the influence of the field of the nuclear quadrupole. Augmentation of standard basis sets with a single set of single-exponent d functions, matched to the reciprocal square of the nominal 1s radius, reduces these errors by up to 90%.

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GRAPHICAL ABSTRACT

Modern quantum mechanical methods are capable of calculating the potential surface and almost all spectroscopic properties of small molecules to an impressive degree of precision. Large correlation-consistent basis sets and sophisticated electron correlation methods can determine the internuclear potential of first row diatomics to a degree of accuracy that lies well within the error introduced by the Born-Oppenheimer approximation; while for some experimentally taxing electrostatic quantities, such as multipole moments, computed properties are probably more accurate than the best experiments.

There is, however, one notable exception. The nuclear quadrupole coupling, that is, the electrostatic interaction between $\text{spin} \geq 1$ nuclei and the electric field gradient at the nuclear site, can frequently be measured to better than 1% accuracy by microwave spectroscopy or molecular beam magnetic resonance, and is also measurable by NMR and NQR. As a simple ground state molecular property, it can be computed by most widely available quantum chemistry packages, using standard basis sets and electron correlation methods. Frequently-encountered discrepancies of 10% or more between quadrupole coupling constant calculations and measurements often lie partly with insufficient basis sets, approximate methods for calculating correlation, and failure to account for zero-point or thermally activated vibrational averaging; these failings are often hard to avoid when calculating large complex systems. However, one would hope that we could at least calculate accurate quadrupole couplings for vacuum phase diatomics by standard methods.

That this is not the case can be demonstrated by a simple example. The quadrupole couplings of lithium hydride and deuteride were measured by the group of Ramsay¹ in the ($v = 0, J = 1$) state; since the quoted error for ${}^7\text{Li}^2\text{H}$ was considerably lower than for ${}^7\text{Li}^1\text{H}$, we will use the latter value: $C_{\text{Qw}} = C_{\text{Q01}} = 348.942 \pm 0.037$ kHz. Based on the estimates of Sundholm *et al.*², the rotational correction from the $J = 1$ to the $J = 0$ state is expected to be of the order of 0.03%, and so it will be ignored for the present. Using the recommended value³ of the quadrupole moment $Q_{\text{Li}} = -4.010$ fm² (see below), and the unit conversion formula⁴ V_{zz} (a.u.) = $C_{\text{Q}}/(eQK_{\text{Q}})$, with $K_{\text{Q}} = -2349647.8$ Hartree⁻¹Bohr²fm⁻²s⁻¹, we obtain an electric field gradient at the lithium site, $q_0 = V_{zz,0}$ averaged over the

ground vibrational state, of 0.0370 atomic units (a.u.). Urban and Sadlej³ did not provide error limits for their recommended value of the quadrupole moment (whose uncertainty likely dominates the value of the EFG), but the standard deviation of the 11 values they averaged leads to an error estimate for $Q_{7\text{Li}}$ of ± 0.06 a.u., or around 1.5 %; this dominates the error in the estimate of q_0 .

s	p	d	f	g	h
0.00712219	0.00921147	0.0215908	0.0481097	0.0774595	0.131919

Table 1: Diffuse function exponents for the Li aug-cc-pV5Z basis set.

Coupled cluster singles doubles (CCSD) values of the EFG for $^7\text{Li}^2\text{H}$ at the consensus⁵ equilibrium bond length r_e of 159.491 pm were computed for a series of augmented, correlation-consistent polarized valence multiple zeta basis sets [aug-cc-pVnZ, $n = (\text{D}, \text{T}, \text{Q}, 5)$], downloaded from the EMSL basis set exchange⁶). Diffuse functions for the cc-pV5Z basis set were obtained by variationally minimizing the energy of Li^- with respect to s, p, d, f, g and h exponents. A similar procedure carried out on the smaller basis sets led to exponents virtually identical to those in the basis set exchange. These exponents are tabulated in Table 1. The computations were adjusted for zero-point motion over the vibrational ground state and centrifugal stretching in the $J = 1$ state by solving the rovibrational Hamiltonian, containing second order rotational/vibrational coupling terms, variationally at the CCSD/aug-cc-pVQZ level, using an order-6 polynomial potential function fit to energies computed at 26 values of the bond-length r spaced in increments of 2 pm from $r = 139.612$ pm to $r = 189.612$ pm, and a harmonic oscillator basis set of 9 eigenfunctions generated using the quadratic force constant.

Averaging over the ground state gave q_{01} , the expectation value of q in the ground vibrational, $J = 1$ rotational state. The value of the rovibrational correction to q_{01} was rather small (-3.70×10^{-4} a.u.). The values of q_{01} thus computed are for $n = 2 - 5$ are shown as red circles. A complete basis set (CBS) extrapolation was done by fitting these four points to the function $q(n) = A + B \exp(-Cn)$. It is shown as the red solid line in Fig. 1.

Fig. 1. (Red filled points) CCSD computed values for q_0 for the $v = 0, J = 1$ state of ${}^7\text{Li}^2\text{H}$, as a function of n , for the Dunning aug-cc-pVnZ basis sets with n from 2 to 5. (Solid red line) CBS extrapolation of these points. (Red dashed line) experimental value of q_0 . (Blue filled points) HF computed values for q_e for ${}^7\text{Li}^2\text{H}$, as a function of n , for the Dunning aug-cc-pVnZ basis sets with n from 2 to 5. (Solid blue line) CBS extrapolation of these points. (Blue dashed line). Value of q_e computed by Sundholm et al. using grid Hartree-Fock methods.

The Dunning basis sets are designed to show well-tempered convergence to a complete basis set (CBS) limit, and indeed, they appear to show good and efficient convergence; unfortunately, the converged value of q_{01} is 13% too high, far in excess of the error. The problem is not an idiosyncrasy of the basis set or correlation method; values calculated using second-order Møller-Plesset perturbation theory (MP2) are almost as high. Consistent with this, Urban and Sadlej showed³ that CCSD accurately handles electron correlation in this rather weakly correlated molecule. Moreover, other basis sets of comparable size show similar results.

That there is no inherent problem with Gaussian basis sets is demonstrated by the work of Sundholm *et al.*². The limiting Hartree-Fock (HF) value of the EFG at the ${}^7\text{Li}$ site was computed using numerical calculations over a large grid; a set of contracted Gaussian type orbitals (GTOs) was then constructed specifically to match these results, and correlation corrections were then obtained. This value was then used to evaluate the ${}^7\text{Li}$ quadrupole moment. In a similar way as above, we calculated the HF q_e for the aug-cc-pVnZ series, and present it also on Fig. 1, comparing it with the value of the EFG computed by grid Hartree-Fock methods by Sundholm *et al.*². It can be seen that the limiting Hartree-Fock value

obtained for the aug-cc-pVnZ series exceeds the grid Hartree-Fock value of Sundholm *et al.*² by almost the same factor as our CCSD value exceeds the experimental value. The problem, therefore, appears not to be a mis-estimate of correlation, but a systematic error arising from the Dunning basis sets themselves.

In what respect do Sundholm *et al.*'s GTOs differ from standard sets? Examination of the exponents and contraction coefficients shows one notable difference; the presence of very tight (large-exponent) d functions in their basis set; these are absent in the standard Dunning basis sets. In fact, it was specifically stated that, in order to obtain good agreement with numerical HF calculations, the exponents of the d functions had to be scaled². Such tight d functions are absent from standard basis sets for an elementary reason; the hydrogenic wavefunction contains no d orbitals with principal quantum number less than 3, and molecular wavefunctions composed of linear combinations of atomic orbitals therefore do not contain them either. Nor, indeed, is there any reason why they should, if the goal is to calculate the energy, internuclear potential, or functions derived from it.

However, in the singular case of quadrupolar nuclei, a fundamental assumption underlying the hydrogenic orbitals breaks down. The potential around a quadrupole nucleus is not spherical, but contains a quadrupolar component. As early as 1950, Sternheimer⁷ showed that the effect of the nuclear quadrupole on the core shells is to mix a small amount of d-like character with the s orbitals, and f-like character with the p orbitals. The so-called Sternheimer antishielding coefficient γ_∞ quantifies the induced polarization for the core electronic shells, which adds to the nuclear quadrupole and results (usually) in an amplification of the effective quadrupole moment, in some cases by factors of 100 or more⁸.

Historically, Sternheimer factors were most often used in lattice computations of electric field gradients, primarily in ionic solids. In principle, such polarization is automatically included in *ab initio* and density functional calculations, with the EFG computed as a sum of contributions from the nuclear point charges and the electron density, usually evaluated⁹ as the first derivative of the energy with

respect to the nuclear quadrupole moment at $Q = 0$. In principle, for a complete basis set, this calculation should be exact at any level of electron correlation obeying the Hellmann-Feynman theorem. Unfortunately, for finite basis sets, accounting for this polarization depends on the ability of the electronic wavefunctions to fully distort in response to the nuclear quadrupole, which in turn depends on the presence of tight functions of the appropriate symmetry in the basis set. This requirement has been noted as early as 1984², and it was noted that such tight functions would also permit highly accurate calculations of electron correlation. In fact, basis sets explicitly designed to permit core-valence correlation are now widely used for computations of small molecules. Unfortunately, using such sets for quadrupole coupling constant calculations comes at a heavy price: for boron fluoride, for example, aug-cc-pCV5Z contains 362 basis functions, compared with 254 in aug-cc-pV5Z. By symmetry, the nuclear quadrupole mixes only d functions into the s subshells and only f functions into the p subshells, whereas core-valence correlation mixes functions of nearly arbitrary symmetry. Since the precision of quadrupole constant calculations in all but the smallest molecules is often limited by basis set incompleteness, expanding the basis set by 40% is not a desirable option.

The major hurdle in adapting Gaussian basis sets to account for core polarization is the near isoergicity of the perturbation. It is a trivial exercise in group theory to prove that the first order energy correction to a pure s or p orbital on introducing a nuclear quadrupole is zero. The extra basis functions cannot therefore be computed using standard variational methods. In order to explore the issue, we computed Hartree-Fock energies and EFGs for lithium hydride as a function of basis set level, adding a single tight d function of variable exponent.

The energies are shown in the upper graph in Fig. 2. At the double zeta level, there is substantial energetic benefit to adding a small-exponent d-function; this presumably acts as an additional polarization function to the valence shell. At higher levels of theory, the additional benefit of adding an extra d function diminishes, to the extent that at aug-cc-pV5Z the function is almost energetically neutral.

Fig. 2: (top) Energy and (bottom) electric field gradient perturbation, in atomic units, for LiH at the Hartree-Fock level, at the experimental bond-length of 159.4912 pm, computed using a aug-cc-pVnZ basis set where $n = 2$ (red), 3 (green), 4 (blue) and 5 (violet), on adding a single extra d function of exponent a . The black line in the bottom plot is the grid Hartree Fock value computed by Sundholm *et al.*²

Note that at values of a above 6 Bohr^{-2} , there is no significant energy change at any level of theory. The ' $a = 0$ ' value actually represents no additional function; as one would expect, adding an extra d function does not perturb the energy in the limit of either $a \rightarrow 0$ or $a \rightarrow \infty$.

In contrast, the effects of the additional function on the EFG are relatively much larger and quite different (Fig. 2, bottom). It is clear that as a function of the exponent a , the EFG decreases rapidly, 'overshooting' the numerical result, and then slowly climbs; just as for the energy, at the asymptotic values of zero and infinity, the EFG should approach the value for the respective basis set without the extra exponent. The extra d function affects the EFG in two ways; aside from the desired effect of permitting core polarization, it contributes to the overall electronic structure, particularly at low levels of

theory, as manifest in the energy perturbation. However, it is clear that the effects of the extra function persist into an exponent range where the effect on the energy is imperceptible. The aug-cc-pVnZ calculations with an extra d function of exponent a converge to the grid Hartree-Fock value of the EFG at $a = (11.34, 10.46, 9.29)$ for $n = (3, 4, 5)$. While this is insufficient to extrapolate to a value of a that would yield convergence to the grid HF value for a complete basis set, on the other hand, the flatness of the dependence of EFG on a for large basis sets also means the choice of an exponent is not critical.

	Li	Be	B	N	O
r_{1s} (Å)	0.186	0.138	0.110	0.078	0.068
a (Bohr ⁻²)	8.09	14.7	23.1	33.8	46.0

Table 2: Nominal 1s radii for the quadrupolar atoms of the first row, from (10), and their inverse square roots used as exponents for the Sternheimer compensated functions used in the present work.

Sternheimer’s original calculations suggested that the peak of the perturbation falls at or near the nominal radius of the 1s function. Since nominal 1s radii have been compiled for all the first row elements, and since using this radius allows us to avoid adding an adjustable parameter to the basis set, we decided to set the exponent a to $r_{1s}^{-1/2}$. We added a single extra d function with this exponent to the aug-cc-pVnZ bases for the first row quadrupolar nuclei Li, B, N and O, nuclei for which there are measured microwave spectroscopic EFG values in diatomics. The nominal 1s radii used are given by Waber and Cromer¹⁰; these values, and the computed exponents used in this research, are given in Table 2. This procedure avoids adding an extra adjustable parameter. Aside from our computational limitations, we chose to study diatomics to avoid the complications of performing a full anharmonic vibrational average coupled with molecular rotation, which is relatively trivial for a diatomic but is much more complex a problem for polyatomic molecules.

We used aug-cc-pVnZ functions for n in the range 2 to 6, for the elements Be – Ne downloaded from the EMSL library⁶; the exponents and contraction coefficients are identical to those implemented in Gaussian-09. Lithium functions were obtained as already described; no cc-pV6Z set is available for that element. Second-order Møller-Plesset (MP2) and CCSD calculations used the standard Gaussian

routines. In general, scratch file size limitations prevented CCSD calculations beyond the aug-cc-pVQZ level; however, since the difference between MP2 and CCSD EFGs appeared to be essentially independent of basis set beyond VTZ, estimates of the CCSD value at the V5Z and V6Z level were obtained by applying adding the difference of the CCSD and MP2 levels at the VQZ level to the computed MP2 values. Errors introduced by this procedure are insignificant. Vibrational and rotational corrections were computed as already described.

We used the Year 2008 recommended values¹¹ for the quadrupole moment; however, since quadrupole moments themselves are usually obtained from electric quadrupole coupling constants and field gradients computed by electronic structure methods, a little further discussion is probably in order here. Pyykkö's recommended value for the ^7Li quadrupole moment is still that of Urban and Sadlej³, which, as already discussed, was obtained using basis sets containing tight d functions, and should therefore fully account for core polarization. Other comparably recent estimates^{12,13} of the ^7Li Q are within this value's error limits. The recommended value for the quadrupole moment of ^{11}B was obtained¹⁴ by complete active set self-consistent field (CASSCF) modeling of the hyperfine splittings in the atomic spectrum of boron in the $^2\text{P}_{3/2}$ state. A combination of basis set and grid methods was used, with up to 9 d functions in the basis set; convergence of all hyperfine parameters down to an accuracy of 1 part in 10^5 was checked. We can be quite confident, therefore, that K shell polarization was adequately taken into account. The recommended value for ^{14}N was obtained¹⁵ by similar methods for N^{2+} , and verified with two other states of the states of the N^+ ion; it has more recently been confirmed¹⁶ by molecular calculations on NP. Finally, the recommended ^{17}O moment was obtained¹⁷ by similar finite element multiconfigurational Hartree-Fock (MCHF) calculations on $\text{O}(^3\text{P}_0)$.

Experimental values for the first row diatomics were obtained as follows. Quadrupole coupling constants were obtained for ^7LiH , ^7LiD and ^7LiF by molecular beam electric resonance^{1,18}. These exceed in accuracy the recommended value of the ^7Li quadrupole moment, which was in fact derived from the ^7LiH and ^7LiD data, along with some other molecules³. It is notable that the theory also reproduces

accurately the experimental deuterium isotope effect on the ^7Li quadrupole coupling. The quadrupole coupling constant for the ground rovibrational state of ^{11}BH was very recently obtained¹⁹ by laser-cooled millimeter wave spectroscopy; that of ^{11}BF by microwave spectroscopy²⁰. The microwave value²¹ of the ^{14}N quadrupole coupling constant of $^{14}\text{NO}^+$ is quite accurate. The quadrupole constant for $^{14}\text{N}_2$, uniquely in this data set, was obtained^{22,23} by nuclear quadrupole resonance on the solid at 0 K; it is only possible to use it because the significant effect of zero-point librations and of intermolecular interactions on the constant were painstakingly removed using intermolecular potentials derived from Raman spectroscopy, and pressure-dependent measurements, respectively. Since there are multiple measurements of the ^{17}O electric quadrupole coupling constant for the ($v = 0, J = 0$) state of $^{12}\text{C}^{17}\text{O}$ and $^{13}\text{C}^{17}\text{O}$, a meta-analysis was conducted as follows; discarding the earliest measurement by Rosenblum and Nethercot²⁴, which has large uncertainties, for $^{12}\text{C}^{17}\text{O}$ we combined the values of $q_{0,0}$ from Frerking and Langer²⁵, Cazzoli *et al.*²⁶ and Klapper *et al.*²⁷, while for $^{13}\text{C}^{17}\text{O}$ we used the values of Klapper *et al.* and Puzzarini *et al.*²⁸. Theory indicated the zero-point averaging of the wavefunction would lead to a minuscule isotope correction, with $q_{0,0}$ for $^{13}\text{C}^{17}\text{O}$ being about 0.04% larger than for $^{12}\text{C}^{17}\text{O}$. This was nonetheless applied, leading to a best experimental value of the quadrupole constant of 4.3220(7) MHz for $^{12}\text{C}^{17}\text{O}$. Finally, the microwave value²⁹ for the quadrupole constant in $^{17}\text{O}_2$ was used directly.

As before, the lines denoting CBS extrapolations are fits to the exponential function $q(n) = A + B \exp(-Cn)$, which has been suggested as an empirical extrapolation to the complete basis set. Experimental values for the electric field gradient are compiled in Table 3, as are the equilibrium bond-lengths (generally calculated from the most recently published Dunning coefficients) and accepted values of the relevant nuclear quadrupole moments used in the calculations. The table allows numerical comparison of computed values, with and without Sternheimer compensation, with experiment.

Fig. 3: (Red filled points) CCSD computed values for q_e , using a standard aug-cc-pVnZ basis set, as a function of n . (Red line) CBS extrapolation of these points. (Blue filled points) CCSD computed values for q_e , using the same basis set plus a single Sternheimer compensation function, obtained as described in the text, as a function of n . (Red line) CBS extrapolation of these points as a function of n . (green line) experimental values (light green rectangles) experimental error limits. The compounds computed are (a) ${}^7\text{LiD}$ (b) ${}^7\text{LiF}$ (c) ${}^{11}\text{BH}$ (d) ${}^{11}\text{BF}$ (e) ${}^{14}\text{NO}^+$ (f) ${}^{14}\text{N}_2$ (g) ${}^{12}\text{C}^{17}\text{O}$ (h) ${}^{17}\text{O}_2$

The efficacy of the core polarization correction is clearest for LiD and LiF, where it amounts to 14.8 and 15.5 % of the total (corrected) field gradients, respectively, and brings the CCSD/CBS computed values to within 1.5% and 2.5% of the experimental value, respectively. The correction is between 4.2 and 4.4% % for BH and BF, and 2.6% to 2.9% for NO⁺ and N₂. and corrected computed values are 0.9 % to 22% % from experiment, closer in three of four cases than the uncorrected values, and once again close to or within experimental error. The single anomaly is for ¹⁷O. The corrections for CO and O₂ are quite small (2.9% and 2.3 %), but in both cases they make concordance with experiment slightly worse, and the CO correction breaks the trend of smaller corrections with higher *Z* values. The set of accurate experimental ¹⁷O¹²C and ¹⁷O¹³C constants available makes experimental error unlikely to be the cause of this discrepancy. It is conceivable the recommended quadrupole constant¹⁷ reported for ¹⁷O is too low; certainly the error limits on it are proportionately wider than ⁷Li, ¹¹B or ¹⁴N, and the authors mentioned the calculations converged slowly. However, it is perhaps more plausible that the high level of electron correlation in CO and O₂ are not adequately treated at the CCSD level, Certainly, the convergence of the CO *q*₀ values looks quite unusual, and it is possible a more accurate treatment of correlation (beyond our current capabilities to compute) may resolve the problem.

To expand the set of elements studied, we have performed calculations also on three molecules for which spectroscopic data exists but for which the quadrupole coupling constant has not been measured: BeH⁺, BeC, and NeH⁺. The convergence of the corrected and uncorrected equilibrium electric field gradients *q*_e are shown in Fig. 5. BeH⁺ has been observed spectroscopically, and relevant rovibrational constants obtained³⁰. It has also been the subject of several theoretical studies (see reference 31 and references cited therein) including computations of its field gradient^{32,33}. All of these computational studies used tight d functions and fall close to our corrected CBS value (Table 5).

Fig. 5: (Red filled points) CCSD computed values for q_e , using a standard aug-cc-pVnZ basis set, as a function of n . (Red line) CBS extrapolation of these points. (Blue filled points) CCSD computed values for q_e , using the same basis set plus a single Sternheimer compensation function, obtained as described in the text, as a function of n . (Red line) CBS extrapolation of these points as a function of n . The compounds computed are (a) BeH^+ (b) BeC (c) NeH^+ .

BeC has a very low lying electronically excited state, approximately 2300 cm^{-1} above $X^3\Sigma^-$, and is therefore a challenge for single-reference quantum methods. It has³⁴ a ground state rotational constant B_0 of 1.162 cm^{-1} , but the complex shape of the potential and sparse experimental data make it difficult to generate an equilibrium bond distance; recent theoretical estimates range between 166 and 169 pm. Our fairly low-level calculations (CCSD/aug-cc-pVQZ) find an equilibrium bond-length of 168.88 pm, falling within that range. The field gradient has previously been computed³⁵ at a CASSCF level as a function of bondlength; the value given in Table 5 is intrapolated from those calculations at our computed bondlength. Note that the basis set used in this paper included a Gaussian with an exponent of 8.0, smaller than we recommend for Be; Fig. 2 suggests this would lead to an overcompensated value of q_e , consistent with a comparison of our value with theirs.

NeH⁺ has been characterized structurally by Fourier-transform infrared emission spectroscopy^{36,37}. ²¹Ne quadrupole coupling constants have been computed as a function of bond-length³⁸, and from these the q_0 value for the ground rovibrational state can be calculated, by reversing the authors' procedure. In this case, our *uncorrected* value agrees with previous work; but examining the basis set used by the authors, it is notable that no tight d functions are included in the basis set (which was originally obtained from Cybulski and Bishop³⁹). Thus, this in fact strengthens our contention of the importance of high-exponent polarization functions.

It is clear the very substantial deviations from experiment or high-level computations for the uncorrected Dunning functions are almost completely removed by adding the single d function as suggested. The magnitude of the correction depends strongly on atomic number; it is largest for ⁷Li and smallest for ¹⁷O. This is a straightforward consequence of the decrease of the 1s polarizability with radius of the shell; in fact, a plot of the relative corrections against Z^{-2} yields a credible straight line of slope close to 1, as in Fig. 6.

It is an obvious consequence of this work that the polarization for the 1s shell along the next (second) row should start very small and decrease still further. However, on this row, the 2s and 2p orbitals are as a general rule treated as core, and there is a similarly inadequate provision for core polarization in standard basis sets. Sternheimer antishieldings also increase dramatically as the principal quantum number of the shell increases. Moreover, polarization of these orbitals will be significantly more complex. Under the influence of a field gradient, there is mixing of f-like character into the p-orbitals as well as d-like character into s orbitals. Moreover, because of the radial node, a 2s Sternheimer compensation function requires at least two Gaussians with coefficients of opposite sign. For the moment, therefore, we can but warn that computations of EFGs for the second row, particularly its early members, using standard basis sets, may contain substantial errors. Even in the first row, our approach is merely a first (albeit effective) step, and it is likely substantial improvements can be achieved, using multigaussian Sternheimer functions, over the simple solution we offer.

Given the improved agreement between computation and experiment for Li through N, and the comparatively low computational cost (about 25% more CPU time are the CCSD/aug-cc-pVTZ level for CO, with proportionately lower cost for larger basis sets), it seems reasonable to recommend these additional d functions be added to basis sets for those elements as a matter of routine, when computing electric field gradients. The situation with oxygen calls for further research; but in any case our results indicate failure to include a Sternheimer correction for oxygen will have little consequence. Another and hardly unexpected consequence of the work is that some effort at estimating basis set incompleteness seems *de rigueur*, since double zeta and even to an extent triple zeta computations are rarely satisfactory; most of the commonly used Pople basis sets fall within this range in terms of their number of contracted and uncontracted functions.

	v	J	r_e (pm)	ref	ν_Q (MHz)	ref	Q (fm ²)	$q_{e,\text{exp}}$ (a.u.)	$q_{e,\text{calc}}$ (a.u.)	$q_{e,\text{corr}}$ (a.u.)
⁷ LiH	0	1	159.4912	5	0.34678(4)	1	−4.01	0.036805	0.041600	0.0362459
⁷ LiD	0	1			0.34894(4)			0.037034	0.041828	0.0364725
⁷ LiF	0	0	156.3857	40	0.4156(4)	18		0.04411	0.05225	0.04523
	1	0			0.4061(6)			0.04310	0.05100	0.04398
	2	0			0.3965(8)			0.04208	0.04979	0.04276
¹¹ BH	0	0	123.217	41	−6.43(5)	19	4.059(10)	0.674	0.687	0.659
¹¹ BF	0	0	126.2712	42	−4.305(2)	20		0.451	0.478	0.458
¹⁴ NO ⁺	0	0	106.3195	43	−6.76(10)	21	2.044(3)	1.408	1.459	1.421
¹⁴ N ₂	0		109.7680	44	± 5.39	23		±1.122	1.169	1.136
C ¹⁷ O	0	0	112.8323	45	4.3220(7)		−2.558(22)	0.7191	0.7114	0.6912
¹⁷ O ¹⁷ O	0	0	120.7527	46	−8.29(5)	29		−1.379	−1.392	−1.361

Table 3: Experimental bond lengths, quadrupole coupling constants, and quadrupole moments¹¹ used in the present work; derived from them are the experimental equilibrium electric field gradient q_e , which is compared with calculated values from complete basis set extrapolation of CCSD/aug-cc-pVnZ computed q_e , and values computed using an extra Sternheimer-compensation d function.

	$r_{e,\text{calc}}$ (pm)	$r_{e,\text{exp}}$ (pm)	$q_{e,\text{calc}}$ (a.u.)	$q_{e,\text{corr}}$ (a.u.)	$q_{e,\text{calc, lit}}$ (a.u.)	Ref.
BeH ⁺	131.49	130.98	0.1127	0.1057	0.1062	32
BeC	168.88		0.0910 ¹	0.0829 ¹	0.0760 ¹	35
NeH ⁺	98.77	99.12	−3.065 ²	−3.019 ²	−3.076 ²	38

Table 4: Computed and experimental bond lengths, and computed quadrupole coupling constants, uncorrected and corrected by adding a tight d function, for three molecules whose q_e values have been previously computed but not measured. ¹ computed at the CCSD/aug-cc-pVnZ computed r_e ² q_0 used instead of q_e .

Finally, it should be noted that core polarization is not a phenomenon resulting purely from the electric quadrupole. In principle, a nuclear magnetic dipole mixes p character into the 1s orbital, and basis functions for the first row similarly lack p functions with appropriate exponents. However, in practical terms this may not be nearly so severe an effect, because magnetic fields in nuclear magnetic resonance spectroscopy are in most cases external in origin, and so the core polarization correction should be similar for the same nucleus regardless of atomic environment. Since chemical shieldings can only be measured relative to other molecules, and since the variation in core orbitals with chemistry is rather small, the effect may affect computations of absolute chemical shieldings far more significantly than relative shieldings (i.e. chemical shifts). Nonetheless, this possibility may bear further investigation.

In conclusion, the purpose of this work was not to achieve the highest level of computational accuracy for the quadrupole couplings of these small molecules — that could be better assured using grid HF methods combined with CASSCF or multi-reference configuration interaction — but to provide a straightforward and computationally cheap way to modify standard, widely used basis sets to adequately account for core polarization, in larger molecules, usable by the working magnetic resonance spectroscopist rather than the computational specialist. Particularly in the early first row, this modest addition to the basis set seems to achieve good accuracy at the CCSD/aug-cc-pVQZ level, and substantially increases the accuracy even of MP2/aug-cc-pVTZ level calculations. The proposed functions, of course, are basis set independent, and could easily be added to Pople-type sets, although even for the first row, the convergence of smaller basis sets with respect to the electric field gradient is problematic for other reasons.

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