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Nuclear quadrupole moments of ^{33}S and ^{35}S

Dage Sundholm
Department of Chemistry, University of Helsinki, Et. Hesperiank. 4, SF-00100 Helsinki, Finland

Jeppe Olsen
Theoretical Chemistry, Chemical Centre, University of Lund, P.O. Box 124, S-22100 Lund, Sweden
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The nuclear quadrupole moments of ^{33}S and ^{35}S are studied using numerical multiconfigurational Hartree-Fock (MCHF) calculations on $\mathrm{S}^-(^2P_{3/2})$. A newly developed finite-element MCHF program allowing very large configuration-interaction expansions is used. The $3p^5$ valence correlation decreases the electric field gradient with about 12%, but core-valence polarization increases the electric field gradient with about 14% of the Hartree-Fock value. The final values for the nuclear quadrupole moments of ^{33}S and ^{35}S become $-0.0678(13)$ and $0.0471(9)$ b, respectively.

I. INTRODUCTION

The nuclear quadrupole moment Q may be obtained by combining the experimentally determined nuclear quadrupole coupling constant eqQ/h with theoretical values for the electric field gradient (EFG) q at the nucleus. By using the accurate conversion factors of Ref. 1, the equation for obtaining Q (in barns, $1\mathrm{b}=10^{-28}\ \mathrm{m}^2$) from the experimental eqQ/h (in MHz) and the theoretical q (in a.u.) becomes

$$Q=-(eqQ/h)/(234.964\,730q)\ . \tag{1}$$

Accurate values for the nuclear quadrupole moments of ^{6}Li and ^{7}Li have been determined by combining the experimental eqQ/h and the theoretically calculated EFG of LiH (Ref. 2) and LiF.[3] The nuclear quadrupole moment of ^{14}N has been obtained by combining atomic and molecular quadrupole coupling constants with theoretically calculated electric field gradients.[4–8]

From a computational point of view, sulfur is more complicated than lithium and nitrogen since the electrons of the open $3p$ shell will polarize the $2p$ electrons. This distortion will contribute significantly to the EFG at the nucleus. To get reliable results, it is necessary to describe valence as well as core-valence correlation effects.

An experimental method for estimating the nuclear quadrupole moment is to combine the experimental eqQ/h with an EFG deduced from the anisotropic magnetic hyperfine parameter (spin-dipolar term) and corrected for quadrupole shielding using a semiempirical Sternheimer correction. This method has been used for determining the nuclear quadrupole moment of ^{14}N with an accuracy of about 4% from the hyperfine structure of N^+ in the $2p3p\ ^1P_1$ state.[9] Recently, Trainham, Jopson, and Larson[10] measured the electric and magnetic hyperfine coupling constants of $^{33}\mathrm{S}^-(^2P_{3/2})$ with an accuracy of 1% and 0.1%, respectively. A nuclear quadrupole moment of -0.07 b for ^{33}S was deduced from the experiment. They used a Sternheimer factor of 1.052 to correct for quadrupole shielding. In the absence of reliable *ab initio* calculations, this is probably the best available value for $Q(^{33}\mathrm{S})$. Earlier values of -0.062 and $-0.084(8)$ b for $Q(^{33}\mathrm{S})$ were deduced from *ab initio* Hartree-Fock calculations on OCS, H_2S, and SO_2 using double-ζ-quality Gaussian basis sets,[11] and from experiment on the $^4F_{9/2}$ and $^4D_{7/2}$ states of S^+,[12] respectively.

In this work, an *ab initio* determination of the nuclear quadrupole moment of ^{33}S is presented by combining the calculated electric field gradient and the measured eqQ/h of Ref. 10. The electric field gradients are calculated using a large-scale numerical multiconfigurational Hartree-Fock (MCHF) method[13,14] based on the complete or restricted active space (CAS or RAS) model.[15,16] The nuclear quadrupole moment of ^{35}S is determined by using the ratio $Q(^{35}\mathrm{S})/Q(^{33}\mathrm{S})=-0.695$.[17]

II. METHODS

In this numerical multiconfigurational Hartree-Fock method the radial parts of the occupied orbitals, Coulomb potentials, and exchange potentials are confined to the interval $[0,R_{\max}]$ and the domain is divided into a number of subdomains, elements, each one containing n_p local basis functions. We currently use Lagrange interpolation polynomials of fourth order ($n_p=5$) as these local basis functions. The Lagrange interpolation polynomials have the value 1 at one grid point and 0 at all the others. With this choice of element functions, the expansion coefficients of the orbitals and potentials become the amplitude of the functions in each grid point.

In this numerical basis we construct an energy function

$$E=\sum_{i,j}h_{ij}\Gamma_{ij}+\tfrac{1}{2}\sum_{i,j,k,l}g_{ijkl}\Gamma_{ijkl}\ , \tag{2}$$

where h_{ij} and g_{ijkl} are the one- and two-electron integrals, respectively, and Γ_{ij} and Γ_{ijkl} are the elements of the one- and two-particle density matrices. The energy is optimized with respect to the expansion parameters of the orbitals, i.e., the amplitude of the orbitals in each grid point, and with respect to the expansion parameters of the configuration state functions, i.e., the configuration-interaction (CI) coefficients, with imposed orthonormality constraints on the occupied orbitals and the CI vector. In the orbital optimization, the optimization parameters constitute the nonredundant set of angles of rotations from the virtual space into the occupied orbitals. In a RAS calculation also some occupied-occupied rotations are nonredundant. In the multiconfigurational self-consistent field (MCSCF) procedure both the orbital and CI coefficients are optimized. The CI problem is solved using a Slater determinant-based direct CI algorithm[18] in $D_{\infty h}$ symmetry. The σ vector is constructed in a Slater determinant basis from a CI expansion in the same basis. For the Davidson diagonalization, the vectors are transformed into the configuration state basis. The coupling between the orbital and CI parameters is partly taken into account by using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton optimization technique.[18,19] When the CI problem is solved, the density matrices of Eq. (2) are constructed from the CI vector. The one- and two-electron integrals are recalculated after every change of the orbitals.

We use both the CAS SCF (Ref. 15) and the RAS SCF (Ref. 18) methods. In the CAS method the orbital space is divided into three subspaces: the inactive, active, and virtual spaces. The inactive orbitals are doubly occupied in all configurations, the virtual orbitals are unoccupied and play their role in the optimization of the occupied ones. A full CI is carried out in the active orbital space. The RAS method is an generalization of the CAS idea. The orbital space in the RAS method is divided into five subspaces: the inactive, virtual, and three active spaces RAS I, RAS II, and RAS III. The inactive orbitals are as in the CAS method doubly occupied in all configurations; the virtual orbitals are used only for optimization of the inactive and active orbitals. A lower limit is given for the allowed number of electrons in RAS I, while an upper limit is given for the allowed number of electrons in RAS III. No separate restrictions are given on the allowed number of electrons in RAS II. The RAS II space is reminiscent of the active space in the CAS method. The RAS I space will normally consist of core- and deep valence shells; the RAS II space consists of valence shells and the shells of RAS III are introduced to allow for dynamical correlation and polarization. The complete numerical procedure is discussed in detail in Ref. 13.

The electric field gradient is evaluated from

$$q=\sum_{i,j}\sqrt{16\pi/5}\langle Y_{l(i)}^{m(i)}|Y_2^0|Y_{l(j)}^{m(j)}\rangle\langle\phi_i|r_j^{-3}|\phi_j\rangle\Gamma_{ij}\ . \tag{3}$$

In Eq. (3), Γ_{ij} are the elements of the one-electron density matrix and Y_l^m are the spherical harmonics.

III. RESULTS AND DISCUSSION

The electron configuration of $S^-(^2P)$ is $1s^2 2s^2 2p^6 3s^2 3p^5$. The experimental EFG, deduced from the magnetic hyperfine parameters and corrected for quadrupole shielding, is 1.6 a.u.[10] This value is equal to

TABLE I. The electric field gradient at the nucleus of $^{33}S^-(^2P_{3/2})$ obtained from the five-electron valence correlation calculations.

Method[a]	Active space[b]	CSF[c]	EFG	Energy
HF[d]	$3s1p//1p$	1	1.6092	−397.538 435
HF	$3s1p//1p$	1	1.6092	−397.538 431
CAS	$3s1p//1s1p$	3	1.6068	−397.539 606
CAS	$3s1p//1s2p$	60	1.4337	−397.566 469
CAS	$3s1p//2s2p$	114	1.4335	−397.566 572
CAS	$3s1p//2s3p$	609	1.4771	−397.569 960
CAS	$3s1p//2s4p$	2216	1.4586	−397.570 592
CAS	$3s1p//2s5p$	6305	1.4639	−397.570 778
CAS	$3s1p//1s1p1d$	140	1.5413	−397.606 257
CAS	$3s1p//1s2p1d$	668	1.4116	−397.629 293
CAS	$3s1p//2s2p1d$	1044	1.4118	−397.629 565
CAS	$3s1p//2s3p1d$	3135	1.4541	−397.632 215
CAS	$3s1p//2s4p1d$	7716	1.4374	−397.632 696
CAS	$3s1p//1s1p2d$	1240	1.5361	−397.610 971
CAS	$3s1p//2s2p2d$	5032	1.4019	−397.634 873
CAS	$3s1p//2s3p2d$	11 428	1.4444	−397.637 505
CAS	$3s1p//3s2p2d$	6796	1.4013	−397.634 914
CAS	$3s1p//1s1p3d$	5255	1.5359	−397.611 325
CAS	$3s1p//1s1p1d1f$	2092	1.5269	−397.617 111
CAS	$3s1p//1s2p1d1f$	5358	1.4017	−397.639 969

[a] HF, Hartree-Fock; CAS, complete active space. The number of grid points is 301.

[b] The double slash separates the inactive and active spaces. For example, in the $3s1p//1s1p$ CAS calculation $3s1p$ shells are kept inactive, while the $1s1p$ are active. All shells are optimized.

[c] Number of CSF's in $D_{\infty h}$ symmetry.

[d] The number of grid points is 201.

TABLE II. The electric field gradient at the nucleus of $^{33}S^{-}(^{2}P_{3/2})$ obtained from the core-valence correlation calculations.

Method[a]	Active space[b]	CSF[c]	EFG	Energy
RAS	$3s1p/1s1p$-$1s1p$	1762	1.4990	−397.580 568
RAS	$3s1p/1s1p$-$2s1p$	3922	1.4997	−397.580 782
RAS	$3s1p/1s1p$-$2s2p$	23 875	1.7725	−397.591 415
RAS	$3s1p/1s1p$-$1s2p$	13 377	1.7709	−397.590 853
RAS	$3s1p/1s2p$-$1p$	7092	1.7342	−397.588 823
RAS	$3s1p/1s2p$-$2p$	37 087	1.7056	−397.592 694
RAS	$3s1p/1s2p$-$3p$	135 085	1.6878	−397.593 433
RAS	$3s1p/2s2p$-$2p$	60 484	1.7072	−397.594 956
CAS	$3s//3p$	1122	1.8772	−397.606 060
CAS	$3s//4p$	56 272	1.6938	−397.632 994

[a] RAS, restricted active space; CAS, complete active space. The number of grid points is 201.

[b] The slash separates the RAS I and RAS II active spaces, while the hyphen separates the frozen and optimized shells. For example, in the $3s1p/1s1p$-$2s2p$ RAS calculation only single excitations are allowed from the frozen $3s1p$ RAS I space. The RAS II space consists of the frozen $1s1p$ and optimized $2s2p$ shells. The frozen shells are obtained from a $3s1p//1s1p$ CAS calculation. The RAS III space is empty.

[c] Number of CFS's in $D_{\infty h}$ symmetry.

TABLE III. Relativistic (Rel.) corrections to $\langle r^{-3}\rangle_{3p}$ calculated in the DF-HF approximation (in a.u.). NR denotes nonrelativistic.

Atom	NR	Rel.	Rel./NR
$S^{-}(^{2}P_{3/2})$	4.0227	4.0260	1.000 83
$Cl(^{2}P_{3/2})$	6.7684	6.7902	1.003 22
$Ar(^{1}S_{1/2})$	8.9743	9.0083	1.003 79

TABLE IV. Contributions to the electric field gradient of S^{-} in the $^{2}P_{3/2}$ state (in a.u.).

Contribution	EFG (a.u.)	Q (b)
Hartree-Fock	1.609	−0.0694
Valence *sp* limit[a]	1.462	−0.0764
d-shell correction[a,b]	−0.033	
f-shell correction[a,c]	−0.010	
Valence value[a]	1.419	−0.0787
Core-valence correlation correction[d]	0.226	
Relativistic correction	0.001	
Final value	1.646	−0.0678

[a] $1s$, $2s$, $3s$, and $2p$ inactive and five active electrons.

[b] Change of the EFG when two d shells are added to the active space.

[c] Change of the EFG when one f shell is added to the active space.

[d] Additional contribution from the $2p$ shell.

TABLE V. The nuclear quadrupole moments of ^{33}S and ^{35}S compared with literature values (in b).

Systems	Theoretical method	$Q(^{33}\mathrm{S})$	$Q(^{35}\mathrm{S})$	Reference
Six molecules	Semiempirical	-0.064	0.045	21
OCS, H_2S, SO_2	HF (DZ basis)	-0.062	0.043	11
$S^+(^4D_{7/2},{}^4F_{9/2})$	Magnetic hfs	$-0.084(8)$		12
$S^-(^2P_{3/2})$	Magnetic hfs[a]	-0.07		10
$S^-(^2P_{3/2})$	Numerical MCHF	$-0.0678(13)$	0.0471(9)	Present work

[a]Includes a Sternheimer correction. The reversed sign was reported in the original paper.

the theoretically determined EFG in the Hartree-Fock approximation. The main valence correlation effects to the EFG will arise from a $3p$ to $3p^*$ excitation, where $3p^*$ is a $3p$ correlating shell, but, as will be seen later in this section, the $2p$ to $2p^*$ correlation effects are as important as the valence correlation.

When numerical methods are used, the number of basis functions per symmetry is equal to the number of grid points. In Table I, one sees that Hartree-Fock calculations with 201 and 301 grid points yield the same EFG, which shows that the basis set truncation error is negligible.

The valence correlation effects to the electric field gradient were determined by adding valence correlation shells of s and p symmetry until the EFG became stationary. The obtained sp limit for the EFG became 1.462(1) a.u. To estimate the effect on the EFG of d and f shells, CAS calculations with d and f shells in the active space were performed. The valence correlating d and f shells reduced the EFG with $-0.033(1)$ and $-0.010(2)$ a.u., respectively. In Table I, the five-electron valence CAS calculations are summarized.

As mentioned earlier, the $2p$ shell may be distorted from the spherical symmetry by the polarization effects of the hole in the $3p$ shell. Excitations from the $2p$ shell to a correlating $2p^*$ shell may be important for the electric field gradient. These correlation effects were studied by using the RAS approach. Starting from a valence CAS calculation, all shells obtained from the CAS calculation are kept frozen. A number of $2p$-correlation shells, which are optimized in the RAS calculation, are added to the active space. The core-polarization effects are estimated by allowing single excitations from the $1s$, $2s$, $2p$, and $3s$ shells. The valence shells from the CAS calculation plus the additional core-correlating shells constitute a full CI space (RAS II space). These RAS results are presented in Table II. To check whether the RAS approach yields reasonable results, CAS calculations with $2p$ included in the active space were performed. In these CAS calculations the number of active electrons is 11, so the size of the CI expansion increases rapidly with the number of active orbitals. The $3s//4p$ CAS calculation yields approximately the same result as the largest RAS calculation. The consistency of these results indicates that the sp limit is reached, and that the contribution from the polarization of the $3s$ shell is small.

The relativistic correction to the EFG is estimated by comparing Dirac-Fock and Hartree-Fock results. These calculations are performed using Desclaux's multiconfiguration Dirac-Fock (MCDF) program.[20] In Table III, the relativistic and nonrelativistic values for $\langle r^{-3}\rangle_{3p}$ of S^-, Cl, and Ar are given. Calculations on Cl and Ar were performed to check the reliability of the average of configuration method. The finite nucleus correction of $\langle r^{-3}\rangle_{3p}$ for S^- is 0.0002 a.u., which may be neglected. The final value for the EFG is obtained by adding the d- and f-shell contributions from the valence correlation calculations to the sp limit of the core-polarization calculations and correcting for relativity. The core-valence correlation correction to the EFG is 0.226(10) a.u. In Table IV, the different contributions to the EFG are shown, and the corresponding nuclear quadrupole moments of ^{33}S are given.

The literature values for $Q(^{33}\mathrm{S})$, deduced from the measured hyperfine constants of $^{33}\mathrm{S}^+$,[12] must have larger error bars than reported. The measured quadrupole coupling constants are 50(7) and 56(7) MHz for the $^4D_{7/2}$ and $^4F_{9/2}$ states, respectively. The accuracy of the experimentally determined nuclear quadrupole moment cannot be more accurate than the sum of the relative errors of the magnetic and electric hyperfine coupling constants. The molecular values for $Q(^{33}\mathrm{S})$ of -0.062, -0.051, and -0.065 b, which are reported in Ref. 11, are obtained from experimental hyperfine coupling constants and Hartree-Fock calculations on OCS, SO_2, and H_2S, respectively. These calculations are performed using a double-ζ-quality basis set, which is too small for a reliable determination of the electric field gradients. Furthermore, the correlation effects, which are shown to be important in this work, are not taken into account in those calculations. In Table V, the present values and those from the literature for the nuclear quadrupole moments, $Q(^{33}\mathrm{S})$ and $Q(^{35}\mathrm{S})$, are compared.

While Trainham, Jopson, and Larson[10] do not discuss the sign of the obtained nuclear quadrupole moment, Bird and Townes[21] conclude that the sign of $Q(^{33}\mathrm{S})$ must be negative. Rothenberg and Schaefer[11] also report negative nuclear quadrupole moments for ^{33}S, deduced from Hartree-Fock calculations and experiments on H_2S, SO_2, and OCS. In this paper it is therefore assumed that the sign of the quadrupole moment reported in Ref. 10 is incorrect.

IV. CONCLUSION

The present calculations illustrate the feasibility of numerical multiconfigurational Hartree-Fock calculations with very large CI expansions. The present MCHF calculations gave a value of 1.646(14) a.u. for the electric field gradient. This value, combined with the experimentally measured quadrupole coupling constant of 26.24(23) MHz,[10] yields a nuclear quadrupole moment of −0.0678(13) b for ^{33}S. By using the ratio $Q(^{33}\mathrm{S})/Q(^{33}\mathrm{S})=-0.695$,[17] the nuclear quadrupole moment of the ^{35}S becomes 0.0471(9) b.

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