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Finite-element multiconfiguration Hartree-Fock calculations of the atomic quadrupole moments of $C^+(^2P)$ and $Ne^+(^2P)$

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The atomic quadrupole moments of the $^2P_{3/2}$ states of the carbon and neon cations are calculated using a finite-element multiconfiguration Hartree-Fock method. The Hartree-Fock value for $Q_{zz}(C^+)$ is 0.5373 a.u., the correlation contribution from 2s and 2p is -0.0316 a.u., and the contribution from 1s is -0.0029 a.u. resulting in a final $Q_{zz}(C^+)$ of 0.5028(5) a.u. For $Q_{zz}(Ne^+)$ the Hartree-Fock value is -0.1964 a.u., the correlation contribution from 2s and 2p is -0.0068 a.u., and the final $Q_{zz}(Ne^+)$ becomes $-0.2032(5)$ a.u. For Ne^+ the contribution from 1s is neglected. The estimated uncertainty is given within parentheses.

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I. INTRODUCTION

The first direct measurement of atomic and molecular quadrupole moments was reported in 1963 by Buckingham and Disch [1]. They obtained the molecular quadrupole moment of CO_2 by measuring the anisotropy in the refraction index induced by an electric-field gradient. Molecular quadrupole moments have also been obtained from the anisotropy of the magnetic susceptibility [2,3], ion-molecule scattering data [4], the second virial coefficients [5,6], collision-induced absorption data [7,8], and quantum-mechanical calculations [9].

Angel, Sandars, and Woodgate [10] reported the first measurement of atomic quadrupole moments. Using atomic-beam apparatus, they deduced the quadrupole moment of $Al(^2P_{3/2})$ from the quadrupole interaction between the atomic quadrupole moment and an external electric-field gradient. Using the same apparatus Sandars and Stewart [11] measured the quadrupole moments of $In(^2P_{3/2})$, $Ne(^3P_2)$, $Ar(^3P_2)$, $Kr(^3P_2)$, and $Xe(^3P_2)$. Miller and Freund [12,13] deduced the atomic quadrupole moment of excited ^3P states of He by measuring the anisotropic diamagnetic susceptibility.

Recently Sturrus *et al.* [14] reported very precise measurements of the molecular quadrupole moment of $H_2{}^+$. They obtained the quadrupole moment of the cation by measuring the fine structure intervals for Rydberg states of the neutral molecule. Similar measurements of the atomic quadrupole moments of $C^+(^2P)$ and $Ne^+(^2P)$ are in progress [15]. To our knowledge there are no other measurements of atomic quadrupole moments.

The purpose of this work is to provide accurately calculated values for the atomic quadrupole moments of $C^+(^2P)$ and $Ne^+(^2P)$ for comparison with experimental values. The finite-element multiconfiguration Hartree-Fock (MCHF) method used in this work has previously been used to calculate accurate values for the atomic quadrupole moments of excited states of Be, Al, In, Ne, Ar, Kr, Xe [16], and Ca [17].

II. COMPUTATIONAL METHODS

The present MCHF method (LUCAS) has previously been discussed in the references [18–21]. It is based on the restricted active space (RAS) [22,23] method which is an adaptation of the complete active space (CAS) method [24,25]. The orbital parameters are optimized using unconstrained optimization methods [26], and the configuration-interaction (CI) coefficients are determined using a Slater-determinant-based direct-CI algorithm [22,23]. In the RAS method the configurations are selected, as in the CAS method, by dividing the orbital space into inactive, active, and secondary (virtual) spaces. The active space is further subdivided into three subspaces: RAS I, RAS II, and RAS III. The RAS I space consists usually of core- and deep-valence orbitals; the RAS II space consists of valence orbitals and the RAS III space contains orbitals introduced to allow for dynamical correlation and polarization. A *lower* limit is given for the number of electrons in RAS I and an *upper* limit is given for the number of electrons in RAS III. There are no explicit restrictions on the number of electrons in RAS II. The RAS II space becomes, as the active space in the CAS method, a full configuration-interaction (FCI) space.

In a core-valence (CV) correlation calculation only single excitations are performed from the core orbitals (RAS I), and the introduction of core-core (CC) correlation by orbital rotations is avoided by freezing the core orbitals. The configurations of a multireference all singles and doublets CI are selected by allowing at most two electrons in the RAS III space and the reference configurations are all configurations obtained by distributing the active electrons in the RAS II orbitals.

The following notations are used for the RAS calcula-

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TABLE I. The total energy (in a.u.) and the atomic quadrupole moment of $C^+(^2P)$ (Q_{zz} in a.u.) as a function of the active space.

Orbital space[a]	Label	Energy (a.u.)	Q_{zz} (a.u.)
2*s*//1*p*(1)[b]	C1	−37.292 224	0.537 29
1*s*//2*s*2*p*1*d*	C2	−37.369 423	0.498 49
1*s*//1*s*1*p*/1*s*1*p*1*d*-1*s*1*p*1*d*1*f*(2)	C3	−37.374 907	0.502 08
1*s*//2*s*2*p*1*d*/-1*s*1*p*1*d*1*f*(2)	C4	−37.375 032	0.502 28
1*s*//1*s*1*p*/1*s*1*p*1*d*-2*s*2*p*2*d*2*f*1*g*(2)	C5	−37.376 241	0.505 17
1*s*//1*s*1*p*/1*s*1*p*1*d*-3*s*3*p*3*d*3*f*2*g*1*h*(2)	C6	−37.376 691	0.505 42
1*s*//5*s*5*p*4*d*3*f*2*g*1*h*-[c]	C7	−37.376 841	0.505 65
1*s*//5*s*5*p*4*d*3*f*2*g*1*h*-[d]	C8	−37.391 985	0.505 68
1*s*(1)/2*s*2*p*1*d*/-3*s*3*p*3*d*(2)	C9	−37.383 091	0.496 73
1*s*//2*s*2*p*1*d*/3*s*3*p*3*d*-(2)[e]	C10	−37.373 306	0.499 70
1*s*(1)/2*s*2*p*1*d*/-4*s*4*p*4*d*(2)	C11	−37.383 426	0.497 76
1*s*//2*s*2*p*1*d*/4*s*4*p*4*d*-(2)[e]	C12	−37.373 443	0.500 82
3*s*2*p*1*d*/-3*s*3*p*3*d*(2)	C13	−37.423 002	0.494 46
1*s*//2*s*2*p*1*d*/3*s*3*p*3*d*-(2)[f]	C14	−37.372 917	0.497 20
3*s*2*p*1*d*/-4*s*4*p*4*d*(2)	C15	−37.424 054	0.496 66
1*s*//2*s*2*p*1*d*/4*s*4*p*4*d*-(2)[f]	C16	−37.373 277	0.499 50

[a] For notation see text.

[b] Hartree-Fock calculation.

[c] Full configuration-interaction calculation.

[d] Quasirelativistic calculation.

[e] Valence full configuration-interaction calculation in the shells of the previous core-valence correlation calculation.

[f] Valence full configuration-interaction calculation in the shells of the previous core-correlation calculation.

tions: inactive orbitals // RAS I orbitals (minimum number of electrons in RAS I)/RAS II orbitals /RAS III orbitals (maximum number of electrons in RAS III). A hyphen in the notation means that all orbitals to the left of it are frozen while those to the right are fully optimized.

The atomic quadrupole moment is usually characterized by the $M_L=L$ component of the wave function and evaluated from

$$Q_{zz}=\sum_{ij}\sqrt{4\pi/5}\,\langle Y^{m(i)*}_{l(i)}|Y^0_2|Y^{m(j)}_{l(j)}\rangle\langle\phi_i|r^2|\phi_j\rangle\Gamma_{i,j}\ . \tag{1}$$

Y^m_l are the spherical harmonics, ϕ is the radial part of the orbitals, and $\Gamma_{i,j}$ are the elements of the one-electron density matrix.

The relativistic corrections are estimated by adding the Darwin and mass-velocity integrals to the one-electron integrals and a nonrelativistic CI with the modified integrals is performed. Spin-orbit effects are neglected.

III. RESULTS AND DISCUSSIONS

The quadrupole moments of C^+ and Ne^+ obtained in the Hartree-Fock (HF) approximation are 0.537 29 and −0.196 41 a.u., respectively. The ^2P states have only one dominating configuration, and the HF values are therefore quite close to the final ones. The valence all singles and doubles limit (valence SD limit) for the quadrupole moments of $C^+(^2P)$ and $Ne^+(^2P)$ were obtained by performing MCHF calculations with systematically increasing size of the orbital space. The reference shells of the SD RAS calculations were optimized in valence CAS calculations. In the CAS calculations (C2 of Table I and Ne2 of Table II), the 1*s* shell was inactive, and the 2*s*, 2*p*,

TABLE II. The total energy (in a.u.) and the atomic quadrupole moment of $Ne^+(^2P)$(Q_{zz} in a.u.) as a function of the active space.

Orbital space[a]	Label	Energy (a.u.)	Q_{zz} (a.u.)
2*s*//1*p*(5)[b]	Ne1	−127.817 814	−0.196 41
1*s*//2*s*2*p*1*d*	Ne2	−127.993 369	−0.204 85
1*s*//1*s*1*p*/1*s*1*p*1*d*-1*s*1*p*1*d*1*f*(2)	Ne3	−128.039 602	−0.201 32
1*s*//2*s*2*p*1*d*/-1*s*1*p*1*d*1*f*(2)	Ne4	−128.045 438	−0.201 99
1*s*//1*s*1*p*/1*s*1*p*1*d*-2*s*2*p*2*d*2*f*1*g*(2)	Ne5	−128.055 775	−0.202 60
1*s*/111*s*1*p*/1*s*1*p*1*d*-3*s*3*p*3*d*3*f*2*g*1*h*(2)	Ne6	−128.061 651	−0.202 57
1*s*//1*s*1*p*/4*s*4*p*4*d*3*f*2*g*1*h*-(2)[c]	Ne7	−128.200 128	−0.202 55

[a] For notation see text.

[b] Hartree-Fock calculation.

[c] Quasirelativistic calculation.

TABLE III. Contributions to the atomic quadrupole moments of C$^+$(^2P) [$Q_{zz}(C^+)$] and Ne$^+$(^2P [Q_{zz}(Ne$^+$)] (in a.u.).

Contribution	$Q_{zz}(C^+)$/(a.u.)	$Q_{zz}(Ne^+)$/(a.u.)
Hartree-Fock	0.537 29	−0.196 41
Valence SD limit[a]	0.505 42	−0.202 57
Contribution from higher excitations	0.000 23	−0.000 67
Relativistic correction	0.000 03	0.000 02
Core-valence correction	−0.003 06	[b]
Core-core and core-valence correction	−0.002 85	[b]
Final value	0.502 8(5)	−0.203 2(5)

[a] 1*s* uncorrelated and all single and double excitations from 2*s* and 2*p*.

[b] For Ne$^+$ the contributions from 1*s* are small and neglected.

3*s*, 3*p*, and 3*d* shells were active. In the subsequent RAS calculations the shells of the C2 and Ne2 calculations are frozen. The 2*s* and 2*p* shells are set in RAS II, while the 3*s*, 3*p*, and 3*d* shells are in RAS III. The RAS III space is augmented by sets of shells which are optimized in the RAS calculations. At most two electrons are allowed in RAS III. See Tables I and II. In the largest RAS calculation the RAS III space consists of a 4*s*4*p*4*d*3*f*2*g*1*h* set of shells. The Q_{zz} obtained in these RAS calculations (C6 and Ne6) are 0.505 42 and −0.202 57 a.u. for C and Ne, respectively.

For C$^+$ it is possible to perform full CI in the valence orbitals and thereby estimate the contribution from triple excitations. For Ne$^+$, that contribution is estimated by comparing the values for Q_{zz} obtained in the Ne3 and Ne4 calculations. In the Ne4 calculation, the RAS II space consists of the 2*s*, 3*s*, 2*p*, 3*p*, and 3*d* shells. The reference space of the Ne4 calculation is large enough that the contributions from the higher-order excitations to the 4*s*, 4*p*, 4*d*, and 4*f* shells may be neglected, and the Q_{zz} of the Ne4 calculation is very close to that of a corresponding FCI calculation. A comparison between the C6 and C7, and the Ne3 and Ne4 calculations shows that for both C$^+$ and Ne$^+$ the higher-order excitations contribute very little to the Q_{zz} (0.045% for C$^+$ and 0.33% for Ne$^+$).

The contribution to Q_{zz} from 1*s* is estimated for C$^+$ by performing both core-valence and core-core correlation calculations in *spd* basis. In the CV calculations, the shells of the C2 calculation are frozen and single excitations are performed from the 1*s* shell in the RAS I space. The 2*s*, 2*p*, and 3*s* and 3*d* shells are in RAS II, while the optimized shells are set in RAS III. Again only two electrons are allowed in RAS III. The CV correlation contribution is estimated as the difference in Q_{zz} obtained in the CV calculation (C11) and the value obtained in a valence CI calculation (C12) performed in the same shells. The size of the RAS III space was increased until the difference between two subsequence values for the CV correlation contribution became small. See Table I.

The core-core correlation calculations are performed in the same way as the core-valence correlation calculations. But now the 1*s* shell is in RAS II and the RAS I space is empty. In the core-core correlation calculation both the core-core and core-valence correlation effects are taken into account. The CC and CV correlation contribution is also estimated by comparing the value for Q_{zz} obtained in the CC correlation calculation (C15) with that of a valence CI calculation (C16) performed in the same basis. The core-valence correlation calculations and the core-core correlation calculations give approximately the same 1*s* contribution to Q_{zz}. The difference between the CV correlation value and the CC and CV correlation value in Table III is the true core-core correlation contribution. For C$^+$, the 1*s* shell contributes only 0.6% to the total Q_{zz}. For Ne$^+$ the 1*s* contribution is expected to be less. Assuming that the relative contribution to the Q_{zz} scales as Z^{-2}, where Z is the nuclear charge, the 1*s* contribution for Ne$^+$ becomes 0.0004 a.u. This is the largest source of uncertainty in the Q_{zz} value for Ne$^+$. The relativistic corrections which do not include spin-orbit splitting effects are very small for both C$^+$ and Ne$^+$. The calculations are summarized in Table III.

IV. CONCLUSIONS

The atomic quadrupole moments of C$^+$($^2P_{3/2}$) and Ne$^+$($^2P_{3/2}$) have been systematically studied using large-scale finite-element MCHF calculations. The HF values for the quadrupole moment of C$^+$ are about 6% larger than the final Q_{zz} of 0.502 8 (5) a.u., and for Ne$^+$, it is in absolute value about 3% smaller than the final Q_{zz} of −0.203 2(5) a.u. The correlation contributions to the Q_{zz} of the $2p^1\,{}^2P$ and $2p^5\,{}^2P$ states are small because there are no near-degeneracy or polarization effects present. Most of the correlation contribution to the Q_{zz} is obtained in the valence all singles and doubles RAS calculation. The 1*s* polarization contribution and relativistic effects are found to be very small.

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