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Core-valence correlation effects on $E1$ and $E2$ decay rates in Ca^+

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Elaborate multiconfiguration Hartree-Fock wave functions have been obtained for the $4s\,^2S$, $3d\,^2D$, and $4p\,^2P^\circ$ states in Ca^+ in order to investigate the core-valence correlation effects on the transition probabilities of the electric dipole ($E1$) and quadrupole ($E2$) processes involving these levels. In parallel, model-potential calculations using a core-polarization potential have been performed. They support the large reduction of the oscillator strengths found in the *ab initio* approach for both the $E1$ and $E2$ processes. The agreement between the two sets of results is satisfactory only if the polarization term is included in the Hartree-Fock variational procedure. The present theoretical $^2P^\circ_{1/2,3/2}$ lifetime values differ by 3.5% from the most recent fast-beam laser measurements with an estimated single-standard-deviation uncertainty of about 1%.

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I. INTRODUCTION

Precise wave functions have been obtained in the multiconfiguration Hartree-Fock (MCHF) scheme for the Ca and Sr alkaline-earth-metal atoms, taking valence correlation effects into account [1,2]. These wave functions were used for evaluating the radiative lifetimes of low-lying levels. The irregularities and departures to simple scaling laws observed in the Sr lifetime trends are reproduced very well by the theoretical calculations and can be explained by strong configuration-mixing effects in the outer valence-electron pair. The same perturbations strongly affect the isotope shifts. The large positive relative residual shifts measured from two-photon experiments in Ca and Sr can be understood qualitatively by these outer correlation effects [3,4]. This approach works less well in Ca than in Sr [2] and, despite the relative success of these studies, core-valence and core correlation need to be considered. These correlation effects can be incorporated either explicitly through a configuration-interaction (CI) or multiconfigurational procedure (MCHF), or by the use of model potentials [5]. The latter approach results in a considerable saving of computer time, compared with the explicit CI scheme, but questions of accuracy are raised and systematic comparisons need to be made. The present paper is a step in this direction, improving in the same way the MCHF−ASP atomic-structure package [6] by including the one-body core-polarization correction. Before tackling the spectroscopy of nominal "two-electron" systems by some hybrid method using the MCHF approach for the valence correlation and a core-polarization potential model for the core-valence correlation effects, it is essential to test the reliability of the latter on nominal "one-electron" systems. Ca^+ is a good candidate not only because core-valence correlation is large but also because a number of accurate experimental measurements have been published recently for this ion.

Accurate determinations of lifetimes for the $4p\,^2P^\circ_{1/2}$ and $4p\,^2P_{3/2}{}^\circ$ states in Ca^+ are now available [7,8]. They involve fast-beam laser excitation which removes the classical cascade problems encountered in beam-foil spectroscopy. These lifetime measurements, with an estimated 1% of accuracy, disagreed at the time of the publication by about 5–9% with all the available *ab initio* values. The situation for Ca^+ was similar to that of neutral lithium and sodium for which an unexplained 1% difference remains between the multiconfiguration Hartree-Fock [9] or many-body perturbation (MBPT) [10] theoretical oscillator strengths and the fast-beam laser experimental values [11] supported recently by accurate time-resolved laser spectroscopy experiments [12,13]. At the same time, recent *semiempirical* calculations based on nonrelativistic Hartree-Fock-Slater wave functions are in agreement with the measurements in lithium [14], along the sodium isoelectronic sequence [15] and for Ca^+ [16]. In this context, it is highly interesting to see what the *ab initio* multiconfiguration Hartree-Fock method and the *ab initio* and semiempirical Hartree-Fock core-polarization model potentials can do for Ca^+. After the present calculations were completed, Guet and Johnson [17] published relativistic many-body-perturbation-theory results through third order; the corresponding excited p lifetimes in Ca^+ agree with measured values within 2% after semiempirical corrections are included. For Ca^+, in contrast to Ba^+ and Sr^+, the agreement is even better (1%) when using the theoretical (i.e., not modified semiempirically) transition amplitudes.

The metastability of the $3d\,^2D_{3/2,5/2}$ levels of Ca^+ is also of theoretical interest. In the singly charged alkali-metal-like ions the metastability of the $(n-1)d\,^2D_{3/2,5/2}$ levels can be understood as a consequence of the d orbital

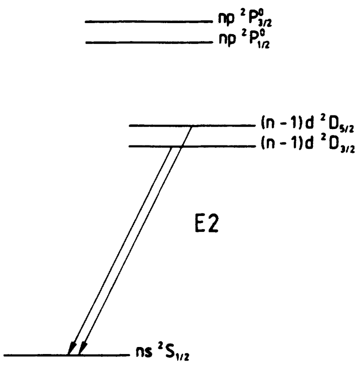

FIG. 1. Level diagram of Ca^+ ($n=4$), Sr^+ ($n=5$), and Ba^+ ($n=6$).

collapse with increasing nuclear charge, accompanied by a corresponding lowering of the ^2D levels until they lie between the $ns\ ^2S$ and $np\ ^2P^\circ$ levels (see Fig. 1). For Ca^+, Sr^+, and Ba^+, these levels can then decay to the ground $ns\ ^2S_{1/2}$ state via an electric quadrupole process. The other $E2$ and $M1$ processes have been shown to be negligible [18]. The very long radiative lifetimes have been measured recently using the ion storage technique [19,20] for Sr^+ $[\tau(^2D_{3/2,5/2})=395$ ns, 345 ns$]$ and Ba^+ $[\tau(^2D_{3/2,5/2})=17.5$ ns, 47 ns$]$. Similar experiments for Ca^+ are planned for the near future [21] and other than the semiempirical MBPT values of Guet and Johnson [17], no recent theoretical prediction is available.

Lastly, the astrophysical interest of the $E2$ $\lambda=7293,7326$ Å lines of Ca^+ arising from the transitions connecting these metastable level components to the ground state is well known. These lines are considered, for instance, by specialists of Seyfert 1 galaxies and T Tauri stars [22] and have been used in a recent study of the Beta Pictoris disk [23].

Elaborate variational wave functions have been calculated for $4s\ ^2S$, $3d\ ^2D$, and $4p\ ^2P^\circ$ of Ca^+ in order to evaluate the oscillator strengths and lifetimes involving these levels. In the "all-electron" approach, in which the core-valence interaction is treated by *explicit* configuration interaction, we investigate the core-polarization effects by opening the $3p^6$ core subshell within the multiconfiguration Hartree-Fock approximation. This method is described in Sec. II. In parallel, the frozen-core Hartree-Fock model including a core-polarization correction (HF+CP), used in a perturbation, variational, or semiempirical scheme, is described in Sec. III. The relativistic effects on the wave functions have been neglected and are introduced into the radiative data only through the use of the experimental frequency factors. The ionization energies, oscillator strengths, and lifetimes calculated in the two different schemes are compared to each other and to the most recent theoretical and experimental values in Sec. IV.

II. MCHF CALCULATIONS

All the calculations were performed using the atomic-structure software package [24,6] based on the multiconfiguration Hartree-Fock approach [25].

A. MCHF wave functions

Ca^+ is an alkali-metal-like system and can be treated at the simplest level as a one-electron system with the nl electron in the nuclear potential $-20/r$ modified by the $1s^22s^22p^63s^23p^6$ core. A frozen-core Hartree-Fock (HF-FC) calculation on (core)nl, taking the core from a Hartree-Fock calculation for the ground state of Ca^{2+}, is a good starting point but neglects the correlation in the motion of the electrons. A recent study of the resonance transition in potassium $4s\ ^2S-4p\ ^2P^\circ$ [9] showed that reasonably accurate oscillator strengths can be calculated using the multiconfiguration approximation including core-valence correlation only with the $3p^6$ core. In Table I we present the MCHF configuration state function (CSF) expansions,

$$\Psi(\Gamma LS)=\sum_i c_i\Phi(\gamma_i LS) \ ,$$

used in the present work. These wave functions have been built using the separated pair approach [25]. The idea is to correlate "separately" each pair which can be formed from the coupling of one $3p$ core electron to the valence electron, using the reduced forms of the MCHF expansions for each pair in the same calculation. For $4s\ ^2S$, for instance, the two pairs to correlate when opening the $3p^6$ subshell are $3p4s\ ^{1,3}P^\circ$. The natural coupling scheme would be $3p^53p4s[^{1,3}P^\circ]\,^2S$, which is transformed into $3p^53p[^{1,3}S]4s\ ^2S$ according to the angular coupling scheme required by the program MCHF−NONH [26] used for calculating the Hamiltonian matrix. Different sets of orthogonal orbitals are used for the different angular couplings (the orbital subscripts designate the different orthogonal sets), but keeping orthogonality between the configuration-state functions. For the $3d\ ^2D$ state, six different electron pairs $3p3d\ ^{1,3}P^\circ, ^{1,3}D^\circ, ^{1,3}F^\circ$ are required for capturing the same effect, increasing the number of radial distributions to optimize. Similarly, for the $4p\ ^2P^\circ$ state, there exist six different pairs, i.e., $3p4p\ ^{1,3}S, ^{1,3}P, ^{1,3}D$, but the situation is somewhat more complex. Indeed, the same $4p$ orbital is used for $4p^2\ ^1S, ^1D, ^3P$ in order to fulfill the orthogonality constraints between the configuration-state functions. Therefore, these three components do not satisfy Brillouin's theorem and it is necessary to include one-electron excitations such as $4p5p\ ^1S, ^1D, ^3P$. The lengths of the expansions used are 17 (^2S), 63 ($^2P^\circ$), and 37 (^2D) involving, respectively, 38, 26, and 78 different radial distributions $P_{nl}(r)$.

The core orbitals $\{1s,2s,\ldots,3p\}$ that arise were obtained in two different ways: MCHF-CV$_1$, from a Hartree-Fock calculation for the ion $3p^6\ ^1S$ of Ca^{2+}, or MCHF-CV$_2$, from a MCHF (2×2) calculation for the ion including the dominant radial correlation effects $\{3p^6+3p^54p\ ^1S\}$.

In the latter approach, the fully variational (2×2) multiconfiguration calculation turned to be extremely unstable. A two-step procedure consisting of (i) optimizing the $1s,2s,2p,3s$ orbitals on the ground state $3p^6\ ^1S$ of Ca^{2+} followed by (ii) optimizing the $3p,4p$ orbitals within the two-configuration approximation $\{3p^6+3p^54p\ ^1S\}$ of Ca^{+2} was used to overcome this convergence difficulty.

The comparison between the two sets of results illustrates the "indirect" effects of core correlation on core-valence correlation. In both types of calculations, MCHF-CV$_{1,2}$ *all* the orbitals outside the core were varied, their number being 33, 21, and 73 for ^2S,$^2P^\circ$, and ^2D, respectively. For the $^2P^\circ$ state, however, no stable solution was found in the MCHF-CV$_2$ approximation using the multiconfiguration superposition of Table I. An "explicit" representation $\{3p^64p_1,5p_1,6p_1\}$ was then used in order to avoid this instability. The "contracted" form

$$c\,3p^64p_3 \equiv 3p^6\{c_14p_1+c_25p_1+c_36p_1\}$$

was used for evaluating the first-order corrections in the transition-matrix elements arising from the inner subshells (see Sec. II B).

In Table II we report the ground state $4s\ ^2S$ MCHF-CV$_{1,2}$ eigenvector compositions, limited to the components larger than 1%. In this table each configuration with its mixing coefficient is followed by the corresponding subshell coupling information specifying the configuration-state function. Note that the electron labels might differ from Table I, the number of nodes in the radial distributions being counted *a posteriori* for determining the associated principal quantum numbers. In an orthogonal scheme in which, for instance, the $4s_1$ and $4s_3$ orbitals would be identical, the $3p \rightarrow p$ one-electron excitations would correct the frozen-core approximation for which Brillouin's theorem does not hold. In both MCHF-CV$_{1,2}$ nonorthogonal approaches, the contributions such as $3p^54p_14s_1$ also capture core-valence correlation effects. However, the wave functions differ considerably between the two MCHF calculations. In MCHF-CV$_2$, the dominant core-valence contribution (10%) corresponds to $3p^54p_1[{}^1S]4s_1$, while the corresponding weight in MCHF-CV$_1$ decreases drastically below 1%. The reason for this eigenvector modification is the difference in the core descriptions and, subsequently, in the roles played by the correlation orbital $4p_1$ in the two calculations. Indeed, in MCHF-CV$_2$, the frozen $3p$ orbital arises from the (2×2) MCHF calculation $\{3p^6+3p^54p\ ^1S\}$ on Ca^{2+} and, therefore, the variational

TABLE I. Multiconfiguration Hartree-Fock (MCHF) expansions for the $4s\ ^2S$, $4p\ ^2P^\circ$, and $3d\ ^2D$ states in Ca$^+$.

LS	Expansion
^2S	$3p^64s_3,3p^5\{4p_1[{}^1S]4s_1,4p_2[{}^3S]4s_2,3d_1[{}^1P]3p_3,3d_2[{}^3P]3p_4,$ $4f_1[{}^1D]3d_3,4f_2[{}^3D]3d_4,4f_3[{}^1G]5g_1,4f_4[{}^3G]5g_2,$ $5p_1[{}^1S]5s_1,5p_2[{}^3S]5s_2,4d_1[{}^1P]5p_3,4d_2[{}^3P]5p_4,$ $5f_1[{}^1D]4d_3,5f_2[{}^3D]4d_4,5f_3[{}^1G]6g_1,5f_4[{}^3G]6g_2\}$
$^2P^\circ$	$3p^64p_3,3p^5\{4p_1^2({}^1S),4p_1^2({}^1D),4p_1^2({}^3P),4p_1[{}^1S]5p_1,$ $4p_1[{}^1D]5p_1,4p_1[{}^3P]5p_1,4p_1[{}^3S]5p_1,4p_1[{}^1P]5p_1,$ $4p_1[{}^3D]5p_1,5p_1^2({}^1S),5p_1^2({}^1D),5p_1^2({}^3P),$ $3d_1^2({}^1S),3d_1^2({}^1D),3d_1^2({}^3P),3d_1[{}^1P]4d_1$ $3d_1[{}^3P]4d_1,3d_1[{}^1D]4d_1,3d_1[{}^3D]4d_1,3d_1[{}^1F]4d_1$ $3d_1[{}^3F]4d_1,4d_1^2({}^1S),4d_1^2({}^1D),4d_1^2({}^3P),$ $4s^2({}^1S),3d_3[{}^1P]4s_3,3d_2[{}^3P]4s_1,4f_2[{}^1D]4p_2,$ $4f_3[{}^3D]4p_4,4d_3[{}^1P]5s_3,4d_2[{}^3P]5s_1,5s^2({}^1S),$ $5d_1^2({}^1S),5d_1^2({}^1D),5d_1^2({}^3P),$ $3d_1[{}^1P]5d_1,3d_1[{}^3P]5d_1,3d_1[{}^1D]5d_1,3d_1[{}^3D]5d_1,$ $3d_1[{}^1F]5d_1,3d_1[{}^3F]5d_1,4d_1[{}^1P]5d_1,4d_1[{}^3P]5d_1,$ $4d_1[{}^1D]5d_1,4d_1[{}^3D]5d_1,4d_1[{}^1F]5d_1,4d_1[{}^3F]5d_1,$ $6p_1^2({}^1S),6p_1^2({}^1D),6p_1^2({}^3P),4p_1[{}^1S]6p_1,$ $4p_1[{}^1D]6p_1,4p_1[{}^3P]6p_1,4p_1[{}^3S]6p_1,4p_1[{}^1P]6p_1,$ $4p_1[{}^3D]6p_1,5p_1[{}^1S]6p_1,5p_1[{}^1D]6p_1,5p_1[{}^3P]6p_1,$ $5p_1[{}^3S]6p_1,5p_1[{}^1P]6p_1,5p_1[{}^3D]6p_1\}$
^2D	$3p^63d_3,3p^5\{4p_1[{}^3S]3d_1,4p_2[{}^1S]3d_2,4p_3[{}^1D]3d_4,4p_4[{}^3D]3d_5,$ $4p_5[{}^1P]3d_6,4p_6[{}^3P]3d_7,4s_1[{}^1P]4p_7,4s_2[{}^3P]4p_8,$ $3d_8[{}^3P]4f_1,3d_9[{}^1P]4f_2,3d_{10}[{}^3D]4f_3,3d_{11}[{}^1D]4f_4,$ $3d_{12}[{}^3F]4f_5,3d_{13}[{}^1F]4f_6,4s_3[{}^1P]4f_7,4s_4[{}^3P]4f_8,$ $4p_9[{}^3D]5g_1,4p_{10}[{}^1D]5g_2,5p_1[{}^3S]4d_1,5p_2[{}^1S]4d_2,$ $5p_3[{}^1D]4d_4,5p_4[{}^3D]4d_5,5p_5[{}^1P]4d_6,5p_6[{}^3P]4d_7,$ $5s_1[{}^1P]5p_7,5s_2[{}^3P]5p_8,4d_8[{}^3P]5f_1,4d_9[{}^1P]5f_2,$ $4d_{10}[{}^3D]5f_3,4d_{11}[{}^1D]5f_4,4d_{12}[{}^3F]5f_5,4d_{13}[{}^1F]5f_6,$ $5s_3[{}^1P]5f_7,5s_4[{}^3P]5f_8,5p_9[{}^3D]6g_1,5p_{10}[{}^1D]6g_2\}$

TABLE II. Comparison of MCHF-CV$_1$ and MCHF-CV$_2$ multiconfiguration Hartree-Fock eigenvectors for the $4s\ ^2S$ state in Ca$^+$. Only contributions of more than 1% are given. The $^{(2S+1)}L$ quantum numbers specify the configuration coupling scheme corresponding to the N shells followed by the $(N-1)$ intermediate quantum numbers.

CSF	MCHF-CV$_1$	MCHF-CV$_2$
$3p^64s_3$ $^1S\,^2S\,^2S$	0.994 037 3	0.947 372 4
$3p^54p_14s_1$ $^2P\,^2P\,^2S\,^1S\,^2S$	−0.038 957 6	−0.307 039 4
$3p^53d_14p_3$ $^2P\,^2D\,^2P\,^1P\,^2S$	0.095 033 0	0.083 438 7
$3p^54f_14d_3$ $^2P\,^2F\,^2D\,^1D\,^2S$	0.017 135 6	0.015 925 7
$3p^54p_24s_2$ $^2P\,^2P\,^2S\,^3S\,^2S$	−0.020 778 1	−0.019 579 7
$3p^53d_24p_4$ $^2P\,^2D\,^2P\,^3P\,^2S$	−0.015 576 6	−0.013 425 4
$3p^55p_15s_1$ $^2P\,^2P\,^2S\,^1S\,^2S$	0.005 691 9	0.012 154 4
$3p^55f_23d_4$ $^2P\,^2F\,^2D\,^3D\,^2S$	0.012 969 6	0.011 313 0

$4p_1$ orbital captures the same core-correlation effects. To illustrate this, we can point out that the weight of $3p^54p_1[^1S]4s_1$ in MCHF-CV$_2$ (0.307) is very close to that of $3p^54p$ in the (2×2) MCHF calculation on Ca^{2+} (0.294), used for providing the core radial distributions. Note that the same difference between MCHF-CV$_{1,2}$ appears, to a lesser extent, for $3p^55p_1[^1S]5s_1$ with the same core coupling as in Ca^{2+} but not for the other coupling, i.e., $3p^54p_2[^3S]4s_2$.

In Table III the MCHF-CV$_2$ eigenvectors are given for the three states. The large magnitude of the $3p^54pnl$ ($nl=4s$, $5p$, $3d$ for ^2S, $^2P^\circ$, and ^2D, respectively) component, already shown in Table II for ^2S, also holds for the $^2P^\circ$ and ^2D states, for the same reasons. The larger components correspond to the usual angular correlation contributions, i.e., *pd*, *df* for ^2S; *sp*, *df* for ^2D; and *sd*, d^2 for $^2P^\circ$. The advantages of the nonorthogonal reduced forms of the multiconfiguration expansions can be appreciated from the overlap matrix elements selected in Table IV, which should be reduced to 1.0 or 0.0 (unit matrix) in the orthogonal scheme along with an increase in the wave-function expansion length.

The huge correlation effects found in the transition

TABLE III. Multiconfiguration Hartree-Fock (MCHF-CV$_2$) eigenvectors for the $4s\ ^2S$, $4p\ ^2P^\circ$, and $3d\ ^2D$ states in Ca$^+$. Only contributions of more than 1% are given. The "collapsed" form of the $4p\ ^2P^\circ$ eigenvector is presented (see text). The $^{(2S+1)}L$ quantum numbers specify the configuration coupling scheme corresponding to the N shells followed by the $(N-1)$ intermediate quantum numbers.

Ca$^+$ $4s\ ^2S$		Ca$^+$ $4p\ ^2P^\circ$		Ca$^+$ $3d\ ^2D$	
$3p^64s_3$ $^1S\,^2S\,^2S$	0.947 372 4	$3p^64p_3$ $^1S\,^2P\,^2P$	0.952 706 4	$3p^63d_3$ $^1S\,^2D\,^2D$	0.934 466 7
$3p^54p_14s_1$ $^2P\,^2P\,^2S\,^1S\,^2S$	−0.307 039 4	$3p^54p_15p_1$ $^2P\,^2P\,^2P\,^3D\,^2P$	−0.150 108 4	$3p^54p_23d_2$ $^2P\,^2P\,^2D\,^1S\,^2D$	−0.345 556 2
$3p^53d_14p_3$ $^2P\,^2D\,^2P\,^1P\,^2S$	0.083 438 7	$3p^54p_1^2$ $^2P\,^3P\,^2P$	0.129 812 6	$3p^53d_94f_2$ $^2P\,^2D\,^2F\,^1P\,^2D$	−0.071 591 8
$3p^54p_24s_2$ $^2P\,^2P\,^2S\,^3S\,^2S$	−0.019 579 7	$3p^54p_15p_1$ $^2P\,^2P\,^2P\,^3P\,^2P$	−0.117 903 6	$3p^53d_{12}4f_5$ $^2P\,^2D\,^2F\,^3F\,^2D$	0.021 456 2
$3p^54f_14d_3$ $^2P\,^2F\,^2D\,^1D\,^2S$	0.015 925 7	$3p^54p_1^2$ $^2P\,^1D\,^2P$	0.094 719 3	$3p^55p_24d_2$ $^2P\,^2P\,^2D\,^1S\,^2D$	0.015 246 1
$3p^53d_24p_4$ $^2P\,^2D\,^2P\,^3P\,^2S$	−0.013 425 4	$3p^54p_15p_1$ $^2P\,^2P\,^2P\,^1D\,^2P$	−0.085 369 3	$3p^54s_14p_7$ $^2P\,^2S\,^2P\,^1P\,^2D$	0.015 096 2
$3p^55p_15s_1$ $^2P\,^2P\,^2S\,^1S\,^2S$	0.012 154 4	$3p^54p_15p_1$ $^2P\,^2P\,^2P\,^1S\,^2P$	−0.071 673 3	$3p^53d_84f_1$ $^2P\,^2D\,^2F\,^3P\,^2D$	0.013 059 2
$3p^55f_23d_4$ $^2P\,^2F\,^2D\,^3D\,^2S$	0.011 313 0	$3p^54p_15p_1$ $^2P\,^2P\,^2P\,^1P\,^2P$	−0.068 050 2	$3p^54s_35f_7$ $^2P\,^2S\,^2F\,^1P\,^2D$	−0.012 026 8
		$3p^54p_15p_1$ $^2P\,^2P\,^2P\,^3S\,^2P$	−0.065 976 5	$3p^54p_33d_4$ $^2P\,^2P\,^2D\,^1D\,^2D$	−0.011 819 9
		$3p^53d_14d_1$ $^2P\,^2D\,^2D\,^1P\,^2P$	0.047 330 1	$3p^54p_44d_5$ $^2P\,^2P\,^2D\,^3D\,^2D$	−0.011 502 2
		$3p^53d_34s_3$ $^2P\,^2D\,^2S\,^1P\,^2P$	0.042 198 2	$3p^54p_14d_1$ $^2P\,^2P\,^2D\,^3S\,^2D$	−0.010 908 3
		$3p^54p_1^2$ $^2P\,^1S\,^2P$	0.040 895 9	$3p^54p_63d_7$ $^2P\,^2P\,^2D\,^3P\,^2D$	−0.010 508 2
		$3p^55p_1^2$ $^2P\,^3P\,^2P$	−0.035 085 3	$3p^54d_95f_2$ $^2P\,^2D\,^2F\,^1P\,^2D$	−0.010 408 9
		$3p^55p_1^2$ $^2P\,^1D\,^2P$	−0.025 694 2		
		$3p^53d_24s_1$ $^2P\,^2D\,^2S\,^3P\,^2P$	−0.017 927 1		
		$3p^55p_1^2$ $^2P\,^1S\,^2P$	−0.011 259 9		

TABLE IV. Selected overlap matrix elements (absolute values) of the MCHF-CV$_2$ radial distributions.

Ca$^+$ ^2S	Ca$^+$ $^2P^\circ$	Ca$^+$ ^2D
$\langle 4s_3 \mid 4s_1\rangle=0.9982$	$\langle 4p_3 \mid 4p_1\rangle=0.9712$	$\langle 3d_3 \mid 3d_2\rangle=0.9914$
$\langle 4s_3 \mid 4s_2\rangle=0.7643$	$\langle 4p_3 \mid 5p_1\rangle=0.2382$	$\langle 3d_3 \mid 3d_9\rangle=0.8694$
$\langle 4s_1 \mid 4s_2\rangle=0.8001$	$\langle 3d_2 \mid 3d_1\rangle=0.5524$	$\langle 3d_3 \mid 3d_{12}\rangle=0.8992$
$\langle 4s_3 \mid 5s_1\rangle=0.0562$	$\langle 4s_1 \mid 4s_3\rangle=0.8670$	$\langle 3d_3 \mid 3d_8\rangle=0.8781$
$\langle 4s_2 \mid 5s_1\rangle=0.5970$		$\langle 3d_3 \mid 3d_4\rangle=0.7724$
$\langle 4p_2 \mid 4p_1\rangle=0.5713$		$\langle 3d_4 \mid 3d_2\rangle=0.8445$
$\langle 3d_2 \mid 3d_3\rangle=0.5573$		$\langle 3d_3 \mid 4d_1\rangle=0.5298$
		$\langle 3d_2 \mid 4d_1\rangle=0.4482$
		$\langle 3d_2 \mid 4d_5\rangle=0.5919$
		$\langle 3d_4 \mid 4d_2\rangle=0.5266$
		$\langle 3d_{12} \mid 4d_2\rangle=0.3342$

probabilities (see Sec. IV) are not expected on the basis of the relatively high purities of the three MCHF-CV$_2$ wave functions (90%, 91%, 87%), which are even purer in the MCHF-CV$_1$ method (99%, 99%, 98%).

B. MCHF oscillator strengths

The MCHF-CV$_{1,2}$ wave functions from Table I are used to calculate the electric dipole and quadrupole oscillator strengths. In a third approach, called hereafter MCHF-CV$_3$, first-order contributions to the transition-matrix elements arising from the $1s^22s^22p^63s^2$ core are determined separately for the shells $3s$ and $2p$, using the MCHF-CV$_2$ variational wave functions and included in the calculation of the final gf values. For instance, for the transition $4s\ ^2S \rightarrow 4p\ ^2P^\circ$, the contribution from the subshell $2p^6$ is evaluated in the following way:

(1) Two multiconfiguration Hartree-Fock expansions,

$$\{2p^63s^23p^64s_3, 2p^53s^23p^64p4s_3, 2p^53s^23p^64p5s_3, 2p^53s^23p^64p3d\ ^2S\}\ ,$$

$$\{2p^63s^23p^64p_3, 2p^53s^23p^64s^2, 2p^53s^23p^64s5s, 2p^53s^23p^64s3d,\ ^2P^\circ\}\ ,$$

are evaluated separately, including all the configuration-state functions arising from the many different couplings of these configurations. Only the $(4p, 5s_3, 3d)$ orbitals for the symmetry ^2S and $(4s, 5s, 3d)$ for the symmetry $^2P^\circ$ are variational, the other orbitals having been taken from the MCHF-CV$_2$ calculations. The choice of these expansions is based on the direct effect of correlation contributions involving the opening of the subshell (here, $2p^6$) and connected through the transition operator to the dominating components of the other symmetry [here, (core)$4s_3\ ^2S$ or (core)$4p_3\ ^2P^\circ$].

(2) The transition probability is then calculated between these two MCHF superpositions and the contribution to the line strength $S^{1/2}$ is renormalized and added to the MCHF-CV$_2$ value.

This procedure is repeated for the subshell $3s^2$, using MCHF expansions judiciously chosen for the first-order contributions to the transition-matrix elements they give rise to.

Finally, let us note that the radial nonorthogonalities resulting from the use of different MCHF orbital sets for the three states optimized separately complicate the transition-matrix element calculations but the expressions remain tractable [27].

III. HARTREE-FOCK+CORE-POLARIZATION CORRECTIONS

Another way of taking core-valence correlation into account is to express the correction to the Hartree-Fock theory in terms of the core polarizability α of Ca^{2+} [28]. The physical picture is one in which the electric field of the valence electron polarizes the core so that the effective potential experienced by the valence electron is changed. We will compare the use of such a core-polarization correction in the Hartree-Fock scheme (HF+CP) with the MCHF approach in which core-valence correlation is included "explicitly."

A. Model potential

By incorporating in the MCHF program the effective core-polarization potential

$$V_{\mathrm{CP}_1}(r) = -\tfrac{1}{2}\alpha_1 \frac{r^2}{(r^2+r_c^2)^3}\ , \tag{1}$$

where α_1 is the dipole polarizability of the core and r_c is a cutoff radius, one can evaluate the core-valence correlation effects on the term energies, using the core from a Hartree-Fock calculation on $3p^6\ ^1S$ of Ca^{2+}. This modification of the effective potential felt by the valence electron can be introduced at two different levels of approximation. In one approach, hereafter referred to as PCP, the core-polarization correction is calculated in a first-order perturbation scheme, as the expectation value of the operator (1). In order to capture more efficiently the core-valence correlation effects, it is tempting to introduce this polarization term into the Hartree-Fock variational procedure. In the latter scheme, called hereafter VCP, the core-polarization correction is not limited only to the energy but also affects the radial distribution of the valence electron. Note already that even if the valence orbitals are unmodified in PCP relative to the frozen-core Hartree-Fock approximation, the corresponding transition probabilities will change according to the specific "correction" of the transition operator introduced and discussed in Sec. III B.

For the PCP and VCP calculations presented hereafter, we opted for the "*ab initio*" electric dipole polarizability value $\alpha_1=3.254(a_0)^3$ calculated by Johnson, Dietman Kolb, and K. N. Huang [29] within the relativistic random-phase approximation. This value agrees very well with the one used by Hameed [30] [$\alpha_1=3.26(a_0)^3$]. The use of the cutoff function appearing in (1) is well known [31,5], but the choice of r_c appears often to be crucial. We have chosen an r_c value fixed to the mean radius of the outermost orbital of the unpolarized corelike ion, i.e., $\langle r\rangle_{3p}=1.2643a_0$. This choice can be justified by the success of this approach adopted by Mohan and Hibbert [32], Hibbert [5], or Migdalek and Baylis [33,34] in other systems. It is interesting to note that the r_c values used by Hafner and Schwarz [35] or by Theodosiou [16], with another cutoff function, are roughly twice our value.

Besides the PCP and VCP model-potential methods, we also investigate the dependence of the results on the adopted r_c value. In a semiempirical treatment, the dipole polarizability α_1 can be found by adjusting the theoretical ionization potential of the ground level to the experimental value, taking the core-polarization correction into account and fixing, for instance, the core-radius value r_c, defining the cutoff function to the mean value of the most external core orbital ($3p$ in our case). Keeping the dipole polarizability value so determined, it is possible to adjust excited energy levels by using r_c as a parameter. This approach was used, for instance, by Migdalek and Baylis [36]. We adopted a similar technique of r_c fitting by adjusting the theoretical ionization energies for the three levels of Ca^+ relative to Ca^{2+} but keeping the *ab initio* $\alpha_1=3.254(a_0)^3$ value. The corresponding results will be labeled SECP. The r_c values so determined are equal to $0.9642a_0$, $1.0365a_0$, and $1.2522a_0$ for $4s\;^2S$, $4p\;^2P^\circ$, and $3d\;^2D$, respectively, and are all lower than the r_c value used in PCP or VCP, giving rise to a larger core-polarization correction in the semiempirical approach with respect to the *ab initio* approach.

The valence-orbital contraction is illustrated in Table V in the core-polarization model. In the variational VCP approach, the largest effect is found for $3d$ (11%), as expected because of the $3d$ collapse. The differences between VCP and semiempirical SECP valence-orbital mean values follow naturally the corresponding r_c changes, the largest effect being found for the $4s$ orbital.

In a study of the electron-impact excitation of Ca^+, Mitroy *et al.* [37] calculated the target wave functions using a semiempirical Hartree-Fock approach including a core-polarization potential. Their method and our SECP approach are very similar. They mainly differ in the form of the cutoff functions used in the way of solving the Hartree-Fock equations, i.e., analytical against numerical.

TABLE V. Mean radius (a.u.) of the valence orbitals from the frozen-core Hartree-Fock (HF-FC), variational (VCP), and semiempirical (SECP) core-polarization calculations.

	$\langle r\rangle_{4s}$	$\langle r\rangle_{4p}$	$\langle r\rangle_{3d}$
HF-FC	3.74	4.55	2.54
VCP	3.66	4.45	2.27
SECP	3.59	4.39	2.26

B. Correction to the oscillator strengths

In the core-polarization model, the $E1$ transitions can be calculated in the length formalism using the correction of Hameed, Herzenberg, and James [28]. In this kind of model, it is well known that corrections to valence-electron transition operators are needed in the evaluation of the transition-matrix elements. The most important corrections of order r^{-3} were derived by Bersuker [38] and Hameed, Herzenberg, and James [28] for the electric dipole operator. When using semiempirical potentials including the long-range polarization force between the electron and the core, Caves and Calgarno [39] generalized the modified multipole moment operator to be used, from a consistent application of the theory. More recently, Laughlin [40] investigated the form of the long-range polarization potential for an atomic system consisting of a spherically symmetric core and valence electrons using the approach of Peach [41] and derived in a "natural" way the higher-order corrections to the transition-matrix elements of the electric multipole operator. The first-order correction of $O(r^{-(2k+1)})$ that he found is consistent with the previously derived expressions. [In Eq. (16) and the following lines of Laughlin [40], the "dipole polarizability" $\alpha(\omega)$ should be replaced by the "multipole polarizability" $\alpha_\nu(\omega)$.] The modified electric multipole Ek transition operator, correct to first order, can be written as

$$\sum_{j=1}^{N_v} r_j^k C_{kq}(\theta_j\varphi_j)\left[1-\frac{1}{r^{2k+1}}\alpha_k\right], \qquad (2)$$

where N_v is the number of valence electrons and α_k is the core multipole polarizability.

In practice, a cutoff function must be introduced in (2) [39]. The cutoff function, consistent with that used in (1), is obtained by replacing $r^{-(2k+1)}\alpha_k$ in (2) by

$$(r^2+r_c^2)^{-(2k+1)/2}\alpha_k\ .$$

For the SECP calculations in which we were using r_c as a parameter, the transition operator should be replaced by the average value of the multipole moments induced by the valence electron in the initial and final states [31,42]. We simply averaged the r_c value over the initial and final states by taking the mean value of the cutoff parameters adopted for both states [36].

TABLE VI. Nonrelativistic (NR) and relativistic (R) binding energies (cm^{-1}) relative to the ionization limit $3p^6\,{}^1S$ of Ca^{2+} in the relaxed-core (HF-RC), frozen-core (HF-FC), multiconfiguration Hartree-Fock (MCHF), and Hartree-Fock with core-polarization (HF+CP) approximations compared to observed values.

Level			HF-RC	HF-FC	MCHF-CV_1^{a}	MCHF-CV_2^{a}	PCP[b]	VCP[b]	(SECP)[b] ≡ (expt.)[c]
Ca^+	$4s\,{}^2S$	NR	91225	91090	96110	95359	93763	93841	
		R	91560	91512	96478	95802	94186	94307	95751.9
Ca^+	$3d\,{}^2D$	NR	75520	73102	84782	81678	81215	81807	
		R	74957	73161	84233	81501	81274	81880	82065.3
Ca^+	$4p\,{}^2P^{\circ}$	NR	67899	67877	70612	69922	69544	69605	
		R	67922	67984	70746	70029	69651	69726	70411.8

[a] Using the multiconfiguration expansions of Table I, MCHF-CV_1, core from $3p^6\,{}^1S$ of Ca^{2+}; MCHF-CV_2, core from $\{3p^6+3p^54p\ {}^1S\}$ of Ca^{2+} (see Sec. II).

[b] PCP, core polarization included as a first-order perturbation correction; VCP, core polarization included variationally; both PCP and VCP with an *ab initio* r_c value; SECP, core polarization included variationally with an r_c value determined semiempirically (see Sec. III).

[c] Binding energies of Edlén and Risberg [60], averaged for spin-orbit splitting.

IV. RESULTS AND DISCUSSIONS

A. Ionization energies

Table VI reports the ionization energies obtained using the relaxed (HF-RC) and frozen-core Hartree-Fock (HF-FC) approaches, the two different MCHF approximations (MCHF-$\mathrm{CV}_{1,2}$), and the two core-polarization models (PCP and VCP), as well as the experimental values (averaged for spin-orbit splitting) used in the semiempirical approach SECP. For each approach, we give the nonrelativistic (NR) and relativistic (R) binding energies, including the relativistic shift corrections (non-fine-structure corrections in the Breit-Pauli scheme). As in neutral K [9], the ionization energy is too large with the core described by a Hartree-Fock calculation for Ca^{2+}. Oppositely, the ionization energy becomes too small with the core described by the two-configuration approximation $\{3p^6+3p^54p\ {}^1S\}$. There is some cancellation between "indirect" core correlation, which can be measured from the differences between the MCHF-CV_1 and MCHF-CV_2 values, and core-valence correlation effects. Starting from the Hartree-Fock model, the increase of the ionization energy values obtained by the inclusion of the core-polarization correction is not large enough and the differences between PCP and VCP results are very small, as far as binding energies are concerned. Among the three states considered here, the $3d\,{}^2D$ state is the more strongly affected by the core-valence correlation in both MCHF and (HF+CP) approaches. This is obviously related to the $3d$-orbital collapse near Ca^+. In the MCHF-CV_2 and VCP approaches, which can be considered as the most reliable *ab initio* methods in the present paper, the inclusion of relativistic shift corrections which never exceed 0.5% improves in most cases the agreement between experimental and theoretical binding energies, the final agreement being very satisfactory, i.e., (0.0,0.7,0.5%) and (1.5,0.2,1.0%) for the ${}^2S,{}^2D,{}^2P^{\circ}$ levels, respectively, in MCHF-CV_2 and VCP.

B. Oscillator strengths

Our HF, MCHF, and (HF+CP) electric dipole ($E1$) and electric quadrupole ($E2$) gf values are reported in Table VII for the transitions connecting the three levels $4s\,{}^2S$, $3d\,{}^2D$, and $4p\,{}^2P^{\circ}$. In all cases, the oscillator strengths are calculated with the experimental rather than the theoretical transition energies in order to avoid any accidental compensation error between the transition-matrix element and the energy factor, reducing in this way the source of error to the line strength only. The comparison of the frozen-(FC) and relaxed-core (RC) results illustrates the large core-relaxation effects, particularly for the two transitions involving the $3d\,{}^2D$ level for which the agreement between the $E1$ and $E2$ length and velocity forms is systematically better when relaxing the core. However, in order to keep the transition probability calculations tractable, the use of a frozen-core description becomes imperative, taking the actual restrictions of the MCHF−ASP program package into account. The inclusion of core one-electron excitations in the multiconfiguration expansion and in the first-order corrections to the transition-matrix elements is, in some way, relaxing this constraint.

In the following, the evaluation of the magnitude of core-valence correlation effects is systematically done, relatively to the frozen-core approximation. If the core-relaxation effects are then classified artificially as core-valence correlation in the frozen-core MCHF scheme, this has the advantage of putting the multiconfiguration and core-polarization results on the same footing, the ionization limit $3p^6\,{}^1S$ of Ca^{2+} being a natural reference.

The convergence of length and velocity formalisms with improving accuracy of the wave functions through the inclusion of more correlation is striking and very satisfactory. In the MCHF scheme, the introduction of core correlation through the MCHF-CV_2 brings the two forms closer to each other for the three transitions considered. The addition to the first-order corrections going from MCHF-CV_2 to MCHF-CV_3 further improves the

TABLE VII. Theoretical oscillator strengths using the length (gf_L) and velocity (gf_V) forms and the observed transition energies, in the relaxed-core (HF-RC), frozen-core Hartree-Fock (HF-FC), multiconfiguration Hartree-Fock (MCHF), and Hartree-Fock with core-polarization (HF+CP) approximations.

	HF-RC	HF-FC	MCHF-CV$_1^a$	MCHF-CV$_2^a$	MCHF-CV$_3^b$	PCP^a	VCP^a	SECP^a
				$4s\ ^2S$–$4p\ ^2P^\circ$				
gf_L	2.37	2.38	1.88	1.96	1.95	2.15	2.04	1.92
gf_V	1.89	1.87	2.07	2.08	2.01			
				$4s\ ^2S$–$3d\ ^2D$				
gf_L (10^{-7})	0.81	1.01	0.62	0.71	0.70	0.99	0.70	0.68
gf_V (10^{-7})	1.05	2.15	0.49	0.83	0.63			
				$3d\ ^2D$–$4p\ ^2P^\circ$				
gf_L	0.78	0.98	0.57	0.65	0.65	0.91	0.66	0.66
gf_V	0.17	0.004	0.79	0.32	0.31			

[a]See footnotes a and b of Table VI for explanations.

[b]The transition-matrix elements were calculated using the MCHF-CV$_2$ wave functions and corrected by first-order contributions (see Sec. II B).

length-velocity agreement for the two transitions involving the $4s\ ^2S$ state but does not affect the $3d\ ^2D$-$4p\ ^2P^\circ$ value. In all cases, the length form looks much more stable than the velocity one. In the same way, the latter is much more sensitive to the first-order corrections calculated in the MCHF-CV$_3$ approach.

For the resonance transition, the 18% reduction of the MCHF-CV$_3$ line strength (length form) relative to the HF value is larger than the 10% found using the core-polarization correction in the PCP model. By including this correction *variationally* (VCP), the reduction becomes larger and converges to the MCHF-CV$_3$ value within 5%.

For the electric quadrupole transition, an even more pronounced effect was found, namely, a reduction of 31%, which is in line with the huge 44% core-valence reduction calculated by Bauschlicher *et al.* [43] for the $E2$ transition $4s3d\ ^2D \rightarrow 4s^2\ ^1S$ in neutral calcium.

Similarly, for the $E1$ transition $3d\ ^2D \rightarrow 4p\ ^2P^\circ$, the core-valence reduction of the length oscillator strength has the same order of magnitude (34% and 32% in the MCHF-CV$_3$ and VCP approaches, respectively). The velocity form is here much more difficult to calculate: The transition integral is affected by strong cancellation effects (the positive and negative parts of the integrand almost cancel), reducing dramatically the one-configuration frozen-core Hartree-Fock value. This kind of abnormally small oscillator strength has been observed already for other alkali-metal-like ions but mainly in the length formalism. Two examples given by Hibbert [44] are the $2s\ ^2S \rightarrow 3p\ ^2P^\circ$ transition in Li I [45] and the $3s\ ^2S \rightarrow 4p\ ^2P^\circ$ transition in Mg II [46] for which even in a CI approach the cancellation of the oscillator strength is very important, the CI expansions being dominated by a single term. The factor 2 between the MCHF-CV$_3$ length and velocity results is noteworthy from that point of view, the "final" velocity value resulting solely from correlation contributions. Note that the cancellation does not occur to the same extent when using the fully variational Hartree-Fock approximation which relaxes the core (HF-RC).

The large core-valence effects on the oscillator strengths found for both transitions involving $3d\ ^2D$ are due to the extreme sensitivity of the $3d$ orbital with respect to the description of the core potential near the collapse. The electric dipole oscillator strengths are compared with other theoretical and with experimental values in Table VIII.

In the set of *ab initio* calculations, Hafner and Schwarz [35] applied a relativistic pseudopotential approach including a core-polarization correction in the transition probability calculation. Guet and Johnson [17] carried out relativistic many-body perturbation theory through third order. The corresponding MBPT values given in this part of the Table have been obtained using their *theoretical* electric transition amplitudes (D^{theor}). The corresponding oscillator strengths are compared with our *ab initio* multiconfiguration MCHF-CV$_3$ results and our VCP values obtained by including variationally the core-polarization potential in the Hartree-Fock procedure.

The core-valence correlation effect found by Hafner and Schwarz is much smaller than what we have found. This smaller reduction can be understood first by the fact that these authors introduced the core-polarization correction in a perturbation scheme and, secondly, because they used a larger r_c core radius value ($r_c = 3.1a_0$ and $1.3a_0$ for the s-p and d-p transitions, respectively) associated with another cutoff function.

The dispersion between the theoretical results is 7% and 48% for the $4s\ ^2S \rightarrow 4p\ ^2P^\circ$ and $3d\ ^2D \rightarrow 4p\ ^2P^\circ$ transitions, respectively. Our MCHF results are much closer to the MBPT results than to the others (1.6% agreement for the resonance transition), but a 13% discrepancy exists between the two sets for the $3d$-$4p$ transition. The VCP values support the MCHF results for the latter transition but are too large for $4s$-$4p$. The difficulty associated with the $3d$-$4p$ transition calculation is corroborated by the larger MBPT semiempirical correction to the transition amplitudes: The ratio $(D^{\text{theor}}/D^{\text{SE}})^2$ amounts to 5% for this transition, while it is only 0.3% for the resonance transition.

In the set of semiempirical results, beside the MBPT

TABLE VIII. Comparison between calculated and measured oscillator strengths in Ca^+.

	ab initio				Semiempirical						Experimental	
Transition	RPP[a]	MBPT[b]	MCHF-CV$_3$[c]	VCP[c]	CA[d]	MP1[e]	MP2[f]	MP3[g]	MBPT[h]	SECP[c]		
$4s$-$4p$	1.03	0.962	0.977	1.019	1.002	1.03	0.961	0.952	0.965	0.959	0.94(7)[i] 1.02(10)[k]	0.955[j]
$4s_{1/2}$-$4p_{1/2}$		0.319	0.324	0.338				0.316	0.320	0.318	0.32(3)[i] 0.34[k]	0.316[j]
$4s_{1/2}$-$4p_{3/2}$		0.643	0.653	0.681				0.637	0.645	0.641	0.66(2)[l] 0.62(4)[i]	0.639[j] 0.68[k]
$3d$-$4p$	0.074	0.0570	0.0646	0.0663	0.0845	0.0714	0.066	0.0574	0.0599	0.066	0.053(6)[l]	
$3d_{3/2}$-$4p_{1/2}$		0.0470	0.0533	0.0547				0.0473	0.0494	0.0547	0.0428[j]	
$3d_{3/2}$-$4p_{3/2}$		0.00956	0.0109	0.0112				0.0096	0.0101	0.0112	0.0088(10)[l]	
$3d_{5/2}$-$4p_{3/2}$		0.0572	0.0649	0.0666				0.0574	0.0601	0.0666	0.053(6)[l]	

[a] Relativistic pseudopotential calculations of Hafner and Schwarz [35].

[b] Relativistic many-body calculations of Guet and Johnson [17] calculated from their *theoretical* transition amplitudes (see text).

[c] Present work: see footnotes a and b of Table VI.

[d] Numerical Coulomb approximation of Lindgård and Nielsen [47].

[e] Semiempirical model potential values of Black, Weisheit, and Laviana [47].

[f] Analytic Hartree-Fock calculations including a semiempirical polarization potential of Mitroy *et al.* [37].

[g] Semiempirical model-potential values of Theodosiou [16] (Hartree-Slater core potential).

[h] Relativistic many-body calculations of Guet and Johnson [17] including semiempirical corrections.

[i] Beam-foil excitation measurements of Andersen *et al.* [50].

[j] Calculated from the fast-beam laser excitation lifetimes [7,8] and the branching ratio of Gallagher [49] (see text).

[k] Electron-beam phase-shift measurements of Smith and Liszt [51].

[l] Hanle-effect measurements of Gallagher [49].

results, which get their semiempirical character from a scaling of Brueckner orbitals, there are the model-potential values of Black, Weisheit, and Laviana [47] neglecting the spin-orbit interaction (MP1) and the results of Theodosiou [16] (MP3) approximating the core potential by the Hartree-Slater method and including a spin-orbit interaction term and the values of Lindgård and Nielsen [48] using an entirely numerical approach to the Coulomb approximation. Lastly, Mitroy *et al.* [37] performed analytic Hartree-Fock calculations including a semiempirical polarization potential (MP2). Their values, corrected with the modified dipole operator, agree perfectly with our SECP results for the two electric dipole transitions. For both transitions, our SECP results are 7% smaller than the values of Black, Weisheit, and Laviana. They agree within less than 1% with the MBPT values of Guet and Johnson and with the results of Theodosiou for the resonance transition, but are significantly larger, respectively, 10% and 15%, for the $3d$-$4p$ transition.

The experimental oscillator strength values were all derived from lifetime measurements using the branching-ratio value

$$R_{\mathrm{br}} = A(^2P^\circ - {}^2S_{1/2}) / \sum_J A(^2P^\circ - {}^2D_J) = 17.6 \pm 2$$

measured by Gallagher [49] without isolating the J components of the $^2P^\circ$ level. The lifetimes have been measured by the Hanle-effect technique [49], the beam-foil excitation technique [50], or the electron-beam phase-shift method [51]. It is also possible to extract the f values from the fast-beam laser excitation lifetimes [7], assuming the same branching ratio R_{br} for the two J components, i.e.,

$$A(^2P^\circ_{1/2} - {}^2D_{3/2}) = \frac{1}{\tau(^2P^\circ_{1/2})(1+R_{\mathrm{br}})} ,$$

$$A(^2P^\circ_J - {}^2S_{1/2}) = \frac{1}{\tau(^2P^\circ_J)(1+R_{\mathrm{br}}^{-1})} .$$

This was done in Table VIII. For the resonance transition, the theory-experiment agreement with the semiempirical values of Theodosiou is perfect. It is also very good with our MCHF results (2%), with the MBPT values (1%), and even better with our SECP results. For the $3d$-$4p$ transition, however, the remaining 11% discrepancy found between the f value calculated from the $^2P^\circ_{1/2}$ lifetime of Gosselin, Pinnington, and Ansbacher [7] and the semiempirical results of Theodosiou is not resolved by our calculations. Our MCHF-CV$_3$, VCP, and SECP values are consistent, though much smaller than the older results, but still 25% larger than the experimental value of Gosselin, Pinnington, and Ansbacher.

This comparison is obviously not strictly rigorous since the experimental f value so derived depends on the branching-ratio value (measured with an accuracy of 11%). In this respect, it is interesting to point out that the latter (17.6±2) is somewhat larger than those which can be calculated from Theodosiou (15.7), Guet and Johnson (15.2), or our transition rates (14.3).

C. Comparison of $E2$ transition probabilities

The electric quadrupole transition probabilities are presented in Table IX. These radiative data were also calculated by Ali and Kim [18] using the relativistic

Dirac-Fock (DF) single-configuration approximation, by Zeippen [22] using CI-type wave functions in the Breit-Pauli approximation (superstructure) in which the one-electron radial orbitals were computed from a Thomas-Fermi statistical model or from the Coulomb potential, and by Guet and Johnson [17] applying the many-body perturbation theory.

The agreement between the superstructure and Dirac-Fock results is satisfactory. In these calculations, the discrepancy has been shown never to overstep 5% for the first six ions of the K isoelectronic series considered, except for Ca^+, where it goes up to 10% [22].

Our nonrelativistic HF transition probability values for the two transitions

$$4s\,^2S_{1/2}-3d\,^2D_{3/2,5/2}$$

differ from each other only through the transition energy factor ΔE_{ij}^5. The effect of the core relaxation in going from HF-FC to HF-RC is huge and our relaxed values in length formalism agree very well with the DF values.

The agreement between the MCHF and (HF+CP) values is remarkable. The 31% reduction found by introducing core-valence correlation effects within both schemes is consistent with the 27% reduction found by Langhoff, Bauschlicher, Jr., and Partridge [52] in neutral K but is larger than the 25% effect found by Zeippen in Ca^+, relative to our frozen-core value. The reduction found by Guet and Johnson [17] is even larger, their values being very close to our MCHF-CV_3 velocity values; this agreement is probably fortuitous in view of the instability of our velocity results with respect to the description of the core (see Table VII). Unfortunately, the magnitude of the semiempirical corrections to the $E2$ transition amplitudes cannot be evaluated from their paper. From all these results, it appears that the old values calculated by Osterbrock [53] ($A=1.30\ s^{-1}$) with a Hartree radial wave function with exchange and by Warner [54] ($A=1.27\ s^{-1}$) are definitely too large.

D. Lifetimes

The lifetimes of the $4p\,^2P^\circ_{1/2,3/2}$ levels calculated from our theoretical (MCHF-CV_3, VCP, and SECP) oscillator strengths are given in Table X and compared with the theoretical results of Cowan and Martinson [55], with the semiempirical values of Theodosiou [16], with the relativistic MBPT results of Guet and Johnson [17] corrected semiempirically, and with the Hanle, beam-foil [including cascade corrections (CC)], and beam-laser experimental values.

The Hartree-Fock-Slater with exchange (HSX) values of Cowan and Martinson [55] include a correlation correction based on a free-electron gas approximation and the agreement with our length MCHF results is rather good (1%). Our set differs from the most recent experimental values of Gosselin, Pinnington, and Ansbacher [7] by about 3.5%. The semiempirical results of Theodosiou are in perfect agreement with these experimental values. The adjusting procedure of the r_c parameter in our variational core-polarization calculations (SECP) improves the agreement with Theodosiou's results (2%), showing some consistency between the two semiempirical approaches. On the other hand, our SECP results agree perfectly with the semiempirical MBPT values of Guet and Johnson but differ from the most accurate lifetimes by 2%. Note that, in the case of Ca^+, the agreement of the MBPT lifetimes with experiment is better (1%) if calculated with the *theoretical* (i.e., not modified semiempirically) transition amplitudes. The corresponding values have been calculated from their Table II as $\tau(^2P^\circ_{1/2})=6.98$ ns and $\tau(^2P^\circ_{3/2})=6.79$ ns. The reasonably good agreement (5%) found between our *ab initio* MCHF-CV_3 and VCP results only supports that core-valence correlation effects can be included to some extent via a variational core-polarization correction.

The lifetimes (in seconds) of the metastable $3d\,^2D_{3/2,5/2}$ levels, calculated from our length MCHF-CV_3 transition probabilities of Table IX, are the following:

	Lifetime(s)
$3d\,^2D_{3/2}$	1.16
$3d\,^2D_{5/2}$	1.14

The very weak J dependency results only from the fine-structure splitting of the ^2D level. In our nonrelativistic approach, the two lifetime values $\tau_{3/2}$ and $\tau_{5/2}$ are differentiated by the frequency factor ω^5, which reflects the $3d\,^2D_{3/2\text{-}5/2}$ fine structure of 61 cm^{-1} [56]. Note that the intraconfiguration $E2/M1$ and the $M1$ $4s\,^2S_{1/2}-3d\,^2D_{3/2}$ decay rates calculated by Ali and Kim [18] and Zeippen [22] turn out to be too small to contrib-

TABLE IX. Electric quadrupole transition probabilities (L = length, V = velocity) for $3d\,^2D_{3/2,5/2}\rightarrow 4s\,^2S_{1/2}$ in Ca^+ using the observed transition energies in the relaxed Hartree-Fock (HF-RC), frozen-core Hartree-Fock (HF-FC), multiconfiguration Hartree-Fock (MCHF), and Hartree-Fock corrected for core-polarization (HF+CP) approximations, compared with other theories.

$A(E2)$ (s^{-1})	HF-RC		HF-FC		MCHF-CV_3^a		VCP[a]	SECP[a]	DF[b]	SPST[c]	MBPT[d]
	L	V	L	V	L	V					
$3d\,^2D_{3/2}-4s\,^2S_{1/2}$	1.00	1.30	1.24	2.67	0.86	0.78	0.86	0.84	1.02	0.93	0.79
$3d\,^2D_{5/2}-4s\,^2S_{1/2}$	1.02	1.32	1.27	2.70	0.88	0.79	0.88	0.86	1.05	0.95	0.81

[a] See footnotes a and b of Table VI for explanations.

[b] Dirac-Fock calculations of Ali and Kim [18].

[c] Superstructure-CI calculations of Zeippen [22].

[d] Relativistic many-body calculations including semiempirical corrections of Guet and Johnson [17].

TABLE X. Lifetimes (ns) of $4p\ ^2P^\circ_{1/2,3/2}$ in Ca^+. Comparison of multiconfiguration Hartree-Fock (MCHF) and Hartree-Fock with core-polarization correction (HF+CP) results with other theoretical estimates and experimental values.

	Theory							
	This work				Other			
	MCHF-CV$_3$[a]		VCP[a]	SECP[a]	Semiempirical	*ab initio*	Experimental	
State	L	V					τ	Method
$4p\ ^2P_{1/2}$	6.83	6.78	6.55	6.93	7.045[b]	6.75[c]	7.07(7)[d]	Beam laser
					6.94[e]	6.44[f]	7.5(5)[g]	Beam foil
							6.62(35)[h]	Beam foil, CC[i]
$4p\ ^2P_{3/2}$	6.64	6.72	6.37	6.74	6.852[b]	6.57[c]	6.87(6)[d]	Beam laser
					6.75[e]	6.28[f]	7.4(6)[g]	Beam foil
							6.68(35)[h]	Beam foil, CC
							6.72(2)[j]	Hanle effect
							6.61(30)[k]	Hanle effect

[a] See footnotes a and b of Table VI for explanations.

[b] Model-potential calculations of Theodosiou [16].

[c] Hartree-Fock-Slater with exchange (HSX) results of Cowan and Martinson [55].

[d] Gosselin, Pinnington, and Ansbacher [7].

[e] Relativistic many-body calculations including semiempirical corrections of Guet and Johnson [17]. The lifetimes calculated from the *theoretical* transition amplitudes (see text) are $\tau(^2P_{1/2})=6.98$ ns and $\tau(^2P_{3/2})=6.79$ ns.

[f] Pseudopotential calculations of Hafner and Schwarz [35].

[g] Andersen *et al.* [50].

[h] Ansbacher, Inamdar, and Pinnington [61].

[i] CC stands for cascade corrected.

[j] Smith and Gallagher [62].

[k] Rambow and Shearer [63].

ute to the ^2D lifetimes. The very recent MBPT theoretical lifetimes of Guet and Johnson [17] (1.27 and 1.24 s for $^2D_{3/2,5/2}$, respectively) agree with ours to better than 10%. This agreement can be qualified as good in comparison with the much smaller theoretical values of Warner [54] (0.80 and 0.77 s, respectively). There is no experimental lifetime value available for these metastable levels. We hope to see our theoretical predictions confirmed through the experiments planned by Werth [21].

It is interesting to note that although the measurement of the ratio $\tau(^2P^\circ_{3/2})/\tau(^2P^\circ_{1/2})$ is very difficult, all the theoretical ratios agree with each other to four decimal places, i.e., 1.0284(2), and agree very well with the most recent experimental ratio [1.029(19)]. The correct value is theoretically simple to obtain: One gets 1.0268 using *any* $S(^2P^\circ\text{-}^2S)$ line strength, the correct (i.e., the observed) λ^3 dependence of the $^2P^\circ_J\text{-}^2S_{1/2}$ transition rates, and neglecting the decays to the ^2D_J states.

V. CONCLUSIONS

Core-valence correlation effects can be incorporated either explicitly through the nonrelativistic multiconfiguration Hartree-Fock method or by the use of a Hartree-Fock model including a core-polarization correction to the potential (HF+CP) [5]. In the first approach, the MCHF results show a strong dependence of the final line-strength value on the description of the core orbitals. It was shown previously that the inclusion of radial correlation *in the core* can be very important for predicting accurate ionization energies and electric dipole transition probabilities [9]. Similar and even larger effects have been found for the electric dipole and quadrupole processes considered in the present study. The core-polarization Hartree-Fock method results in a considerable saving of computer time, compared with the explicit configuration-interaction scheme, but questions of accuracy need to be resolved and systematic comparisons need to be made. The present paper is a step in this direction.

In a recent review of oscillator strength calculations for medium to heavy ions in which the influence of the core on the valence electrons has been treated by the use of model potentials, Hibbert [5] concluded that core polarization with model potentials is of comparable accuracy to that from explicit configuration interaction. The present paper shows that this also holds for Ca^+ but only when the core-polarization correction is included in the effective potential during the variational procedure. The better than 5% agreement found between the MCHF and VCP results is probably good enough to support the use of a combined (MCHF+CP) approach for reinvestigating the spectroscopy of nominal two- [1,2,4] or three-electron systems, though in such systems a two-body core-polarization correction must be included as well. Another good candidate for such a hybrid method is the negative ion Ca^- for which quantum chemistry codes predict that the binding of the $4p$ electron found in numerical MCHF calculations [57] and supported by recent observation [58] disappears when adding core polarization.

It has been shown that our semiempirical core-polarization (SECP) results agree closely with the *ab initio* MCHF calculations for the *three* transitions. In the core-polarization model-potential scheme, this approach has the advantage of avoiding the arbitrariness in the choice of the r_c parameter appearing in the cutoff function. A more systematic study involving other states and systems needs to be done before definite conclusions about the reliability of this approach can be made.

The theoretical $4p\ ^2P^\circ_{1/2,3/2}$ lifetime values calculated by Guet and Johnson, using relativistic many-body perturbation theory through third order and including semiempirical corrections, disagree by about 2% with the most recent fast-beam laser excitation measurements with an estimated single-standard-deviation of about 1%. A slightly larger theory-experiment disparity (3.5%) is found with our *ab initio* nonrelativistic MCHF values. Thus, the original deviation between theory and experiment has been reduced considerably but not removed completely. A similar situation occurs, as mentioned in the Introduction, for neutral lithium [59] and sodium [10], for which an unresolved difference between MBPT calculations and benchmark measurements remains. In our approach, the J dependence of the lifetimes is induced only through the experimental transition energy factors. It would be interesting to investigate if taking the relativistic effects on the wave functions into account within the Breit-Pauli approximation could resolve the remaining discrepancies, though relativistic effects would be expected to be small in lithium.

The comparison of oscillator strengths shows that the $3d$-$4p$ transition rates, which contribute for less than 7% to the $^2P^\circ$ lifetimes, are particularly difficult to calculate. All the theoretical branching ratios are somewhat smaller than the measured value and it would be interesting to have a more accurate branching-ratio measurement to convert the experimental benchmark J-dependent lifetimes into oscillator strengths.

Our MCHF-SECP electric quadrupole transition rates agree with the recent MBPT values of Guet and Johnson to within 10%. There is a need of lifetime measurements for these long-lived metastable levels for which no experimental value is available.

Work of Laughlin [64] has recently appeared in print. Laughlin has used a model-potential approach similar to Theodosiou's but neglecting the relativistic corrections. The semiempirical value for the lifetime of the $4p\ ^2P^\circ$ state presented in this paper ($\tau = 6.67$ ns) agrees very well with our *ab initio* result in the length formalism ($\tau_{\text{MCHF-}CV_3} = 6.70$ ns).

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