Relativistic semiempirical-core-potential calculations in Ca^+, Sr^+, and Ba^+ ions on Lagrange meshes

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Relativistic atomic structure calculations are carried out in alkaline-earth-metal ions using a semiempirical-core-potential approach. The systems are partitioned into frozen-core electrons and an active valence electron. The core orbitals are defined by a Dirac-Hartree-Fock calculation using the GRASP2K package. The valence electron is described by a Dirac-like Hamiltonian involving a core-polarization potential to simulate the core-valence electron correlation. The associated equation is solved with the Lagrange-mesh method, which is an approximate variational approach having the form of a mesh calculation because of the use of a Gauss quadrature to calculate matrix elements. Properties involving the low-lying metastable $^2D_{3/2,5/2}$ states of Ca^+, Sr^+, and Ba^+ are studied, such as polarizabilities, one- and two-photon decay rates, and lifetimes. Good agreement is found with other theory and observation, which is promising for further applications in alkalilike systems.

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I. INTRODUCTION

Atomic polarizabilities and forbidden transitions are of much interest due to their various applications, e.g., in optical atomic clocks, which are based on transitions involving long-lived metastable states [1,2]. Experiments in this field have reached such a high accuracy that relativistic effects are visible and must be precisely accounted for in the calculations [3–14]. Today's most advanced atomic clocks report relative systematic frequency uncertainties below 10^{-17} [15,16]. Reaching higher accuracy is limited by small energy shifts resulting from blackbody radiation and the quadratic Stark effect [5,10,12], highly dependent on the accuracy of static and dynamic polarizabilities [1].

Singly ionized calcium (Ca^+), strontium (Sr^+), and barium (Ba^+) have been proposed as candidates for optical frequency standards due to the long lifetime of their $^2D_{3/2,5/2}$ states [2]. Numerous experiments have been performed in these alkaline-earth-metal ions [17–33]. Additionally, several theoretical studies have been carried out using many-body approaches [4,9–11,34–37]. The estimation of these lifetimes involves the study of the competition between the one-photon electric quadrupole ($E2$) and magnetic dipole ($M1$) channels and the two-photon electric dipole ($2E1$) transitions. While the $E2$ and $M1$ decay rates are widely studied, to our knowledge only one prior calculation [38] of $2E1$ decay rates of the $^2D_{3/2,5/2}$ states has been carried out in these ions.

Ab initio methods include electron correlation through explicit electron excitations. The codes based on these approaches enable the calculation of various spectroscopic properties [39–41]. However, the computational task is important, requiring the diagonalization of large matrices. By contrast, methods introducing a semiempirical core potential simulate the core-valence correlations for an atom with few valence electrons by means of a core-polarization (CP) potential, offering reduced computational times [1,42,43]. The CP potential is tuned to ensure that the energies of the valence electrons reproduce the observed binding energies. Relativistic semiempirical-core-potential calculations of lifetimes and polarizabilities have been performed in Ca^+ [4] and Sr^+ [9], but no such work exists in Ba^+.

The present work combines a semiempirical-core-potential Dirac-Hartree-Fock approach (DHFCP) and the Lagrange-mesh method (LMM) [44,45] to study relativistic polarizabilities, one- and two-photon decay rates, and associated lifetimes in Ca^+, Sr^+, and Ba^+ ions. The LMM is an approximate variational approach involving a basis of Lagrange functions related to a set of mesh points associated with a Gauss quadrature [44–46]. Lagrange functions are continuous functions that vanish at all points of the corresponding mesh but one. The principal simplification appearing in the LMM is that matrix elements are calculated with the Gauss quadrature. The one-body potential matrices are then diagonal and only involve values of the potential at mesh points.

Recently, we have shown that numerically exact solutions of the Dirac-Coulomb equation are obtained with the LMM [45,47]. The method is accurate for most central potentials, such as Yukawa potentials [47]. It also allows the accurate calculation of polarizabilities and of one- and two-photon decay rates in various types of potentials with small computing times [48,49]. In this work, the core orbitals obtained from a

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closed-shell Dirac-Hartree-Fock (DHF) calculation with the GRASP2K package [50,51] are projected on Lagrange bases, contrary to Refs. [4] and [9] where a DHF program was developed using B splines or S-spinors. The DHFCP-LMM method is used for single-valence-electron calculations.

In Sec. II, the formulation of the DHFCP method is recalled, and relativistic expressions of polarizabilities and of one- and two-photon decay rates are presented in the case of a single valence electron in a DHFCP potential. In Sec. III, the principle of the LMM is summarized and the studied properties are approximated with Gauss quadratures. Section IV reports numerical results for low-lying states in Ca^+, Sr^+, and Ba^+, and analyzes the accuracy of the semiempirical-core-potential approach by comparison with *ab initio* calculations and experimental data. Section V contains conclusions.

We use for the fine-structure constant and the atomic unit (a.u.) of time the 2014 CODATA recommended values $1/\alpha = 137.035\,999\,139$ and $\hbar/E_h = 2.418\,884\,326\,509 \times 10^{-17}$ s [52].

II. RELATIVISTIC FORMULATION

A. Closed-shell DHF equations and core orbitals

The starting point of the present approach is a DHF calculation for the closed-shell core state of the atoms. In a.u., the Dirac-Coulomb Hamiltonian for N_{el} electrons in a central field for a point nucleus of charge Z is given by [39]

$$H_{\mathrm{DC}} = \sum_{i=1}^{N_{\mathrm{el}}} \left[c\boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + (\beta_i - 1)c^2 - \frac{Z}{r_i} \right] + \sum_{i<j}^{N_{\mathrm{el}}} \frac{1}{r_{ij}}, \tag{1}$$

where c is the speed of light and $\boldsymbol{\alpha}$ and β are the (4×4) Dirac matrices. Since, in the present work, the DHF method is applied to the ground state of closed-shell ions, the total symmetry J^{Π} is equal to 0^+, with J denoting the total electronic angular momentum and Π the parity. For such systems, the total wave function corresponds to a single configuration state function (CSF), constructed using antisymmetrized products of Dirac spinors

$$\phi_{n\kappa m}(\boldsymbol{r}) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\hat{r}) \\ i\,Q_{n\kappa}(r)\chi_{-\kappa m}(\hat{r}) \end{pmatrix}, \tag{2}$$

involving the large and small radial components, $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$, respectively. The spinor spherical harmonics $\chi_{\kappa m}(\hat{r})$ are common eigenstates of $\boldsymbol{L}^2$, $\boldsymbol{S}^2$, $\boldsymbol{J}^2$, and J_z with respective eigenvalues $l(l+1)$, $3/4$, $j(j+1)$, and m, where $j = |\kappa| - \frac{1}{2}$ and $l = j + \frac{1}{2}\,\mathrm{sgn}\,\kappa$. The quantum number n labels the different states with the same κ symmetry.

The energy of the closed-shell ion is expressed through one-electron integrals I and two-electron Slater integrals R^k as [39,53]

$$\begin{aligned} E_{\mathrm{core}} = {} & \sum_a q_a\, I(a,a) + \sum_a \frac{1}{2} q_a(q_a - 1) \left[R^0(aa,aa) - \frac{[j_a]}{2j_a} \sum_{k=2}^{2l_a} \langle j_a || \boldsymbol{C}^{(k)} || j_a \rangle^2 R^k(aa,aa) \right] \\ & + \sum_{a,b>a} q_a q_b \left[R^0(ab,ab) - \sum_{k=|l_a - l_b|}^{l_a + l_b} \langle j_a || \boldsymbol{C}^{(k)} || j_b \rangle^2 R^k(ab,ba) \right], \end{aligned} \tag{3}$$

where the notation $[j]$ means $(2j+1)$, and contributions to the sums over k are not null when $l_a + l_b + k$ is even. Indices a and b refer to one-electron orbitals $n_a\kappa_a$ and $n_b\kappa_b$, respectively, and q_a is the occupation number of orbital a.

The one- and two-electron integrals appearing in Eq. (3) are respectively given by

$$\begin{aligned} I(a,a) = \int_0^\infty \Bigg[& -\frac{Z}{r} P_a^2(r) + c P_a(r) \left(-\frac{d}{dr} + \frac{\kappa_a}{r} \right) Q_a(r) \\ & + c Q_a(r) \left(\frac{d}{dr} + \frac{\kappa_a}{r} \right) P_a(r) + \left(-\frac{Z}{r} - 2c^2 \right) Q_a^2(r) \Bigg] dr \end{aligned} \tag{4}$$

and

$$\begin{aligned} R^k(ab,cd) = {} & \int_0^\infty \int_0^\infty [P_a(r_1)P_c(r_1) + Q_a(r_1)Q_c(r_1)] \\ & \times \frac{r_<^k}{r_>^{k+1}} [P_b(r_2)P_d(r_2) + Q_b(r_2)Q_d(r_2)] dr_1 dr_2, \end{aligned} \tag{5}$$

where $r_<$ $(r_>)$ denotes the minimum (maximum) of r_1 and r_2. The one-electron radial orbitals used to construct the single CSF are determined variationally so as to leave E_{core}, and additional terms for preserving their orthonormality, stationary with respect to their variations. The resulting coupled radial equations are solved iteratively within the self-consistent field procedure by means of finite difference techniques on an exponential grid [41]. The DHF program used in this work is implemented in the GRASP2K package [50,51].

B. DHFCP Hamiltonian and valence orbitals

Within the frozen-core approximation [39,54], where the relaxation of the core is neglected, the radial DHFCP equation for a single valence electron, denoted by the subscript $v \equiv n_v\kappa_v$ in the following, is given by

$$H_{\mathrm{DHFCP}}\, \phi_v(r) = \varepsilon_v^{\mathrm{DHFCP}}\, \phi_v(r), \tag{6}$$

where $\varepsilon_v^{\mathrm{DHFCP}}$ is the energy of the valence electron. The Hamiltonian H_{DHFCP} reads

$$H_{\mathrm{DHFCP}} = \begin{pmatrix} -Z/r & c\left(-\frac{d}{dr} + \frac{\kappa_v}{r}\right) \\ c\left(\frac{d}{dr} + \frac{\kappa_v}{r}\right) & -Z/r - 2c^2 \end{pmatrix} + V_{\mathrm{core}}(r) \tag{7}$$

and acts on a two-component radial wave function $\phi_v(r) = (P_v(r)\ Q_v(r))^T$, where the superscript T means transposition.

The semiempirical core potential $V_{\mathrm{core}}(r)$ appearing in Eq. (7) is defined as the single-electron operator

$$V_{\mathrm{core}}(r) = V_{\mathrm{dir}}(r) + V_{\mathrm{exc}}(r) + V_{\mathrm{CP}}(r), \tag{8}$$

where, in the case of the interaction with a closed-shell core (core electrons are denoted by the subscript $c \equiv n_c\kappa_c$ in the following), the direct and exchange potentials $V_{\mathrm{dir}}(r)$ and $V_{\mathrm{exc}}(r)$ are defined by their matrix elements [9,39,55],

$$\langle v|V_{\mathrm{dir}}|v\rangle = \sum_{c\in\mathrm{core}} [j_c]\, R^0(vc,vc), \tag{9}$$

$$\langle v|V_{\mathrm{exc}}|v\rangle = -\sum_{c\in\mathrm{core}}\sum_k [j_c] \begin{pmatrix} j_c & k & j_v \\ 1/2 & 0 & -1/2 \end{pmatrix}^2 R^k(vc,cv). \tag{10}$$

The core-polarization potential $V_{\mathrm{CP}}(r)$ has been introduced to simulate the core-valence correlation neglected in the DHF approximation [56–59]. The electric field of the valence electron polarizes the core, which acquires an induced dipole moment proportional to the core static dipole polarizability $\alpha_1(\mathrm{core})$ interacting with the valence electron [56–59]. The potential $V_{\mathrm{CP}}(r)$ is written as

$$V_{\mathrm{CP}}(r) = -\frac{\alpha_1(\mathrm{core})}{2r^4}\left[1 - \exp\left(-r^6/\rho_\kappa^6\right)\right], \tag{11}$$

where ρ_κ is a cutoff parameter that is tuned to reproduce the experimental binding energy of the lowest state of each κ symmetry, and $1 - \exp(-r^6/\rho_\kappa^6)$ is a cutoff function regularizing $V_{\mathrm{CP}}(r)$ at the origin [4]. Expression (11) can be extended by taking higher-order corrections into account [9].

The present semiempirical approach implies corrections to operators. In particular, when computing matrix elements of 2^λ-pole transitions between states $n_a\kappa_a$ and $n_b\kappa_b$, the radial transition operator needs to be modified as [4,9,56,60]

$$\tilde{r}^\lambda = r^\lambda - \frac{\alpha_\lambda(\mathrm{core})}{r^{\lambda+1}}\sqrt{1 - \exp\left[-r^{2(\lambda+2)}/\bar{\rho}^{2(\lambda+2)}\right]}, \tag{12}$$

where $\alpha_\lambda(\mathrm{core})$ is the static multipole polarizability of the core and $\bar{\rho}$ is the average value $\bar{\rho} = (\rho_{\kappa_a} + \rho_{\kappa_b})/2$.

C. Polarizabilities

The static polarizability of an atomic system can be separated into two terms: a dominant first term from the intermediate valence-excited states $\alpha(v)$ and a smaller second term from the intermediate core-excited states $\alpha(\mathrm{core})$ [12]. The latter is smaller than the former by several orders of magnitude [1].

For an atomic system described with Eq. (6), the dipole polarizability $\alpha_1(n_v\kappa_v m_v)$ of a state $n_v\kappa_v m_v$ with angular momentum $j_v > 1/2$ depends on the magnetic projection m_v [1]. It is given by

$$\alpha_1(n_v\kappa_v m_v) = \alpha_1^S(v) + \alpha_1^T(v)\,\frac{3m_v^2 - j_v(j_v+1)}{j_v(2j_v-1)}. \tag{13}$$

The quantity $\alpha_1^S(v)$ is the scalar polarizability while $\alpha_1^T(v)$ is the tensor polarizability in j representation. The 2^λ-pole scalar polarizability reads [1,9,48]

$$\alpha_\lambda^S(v) = \sum_{\kappa'_v} \frac{2[j'_v]}{[\lambda]} \begin{pmatrix} j'_v & \lambda & j_v \\ -1/2 & 0 & 1/2 \end{pmatrix}^2 \mathop{\sum\!\!\!\!\!\!\!\int}_{n'_v} \frac{\left\{\int_0^\infty [P_v(r)P_{v'}(r) + Q_v(r)Q_{v'}(r)]\tilde{r}^\lambda\, dr\right\}^2}{\varepsilon_{v'} - \varepsilon_v}, \tag{14}$$

with the subscript $v' \equiv n'_v\kappa'_v$. The radial functions $P_v(r)$, $Q_v(r)$ and $P_{v'}(r)$, $Q_{v'}(r)$ are solutions of Eq. (6) with respective energies ε_v and $\varepsilon_{v'}$. The sum over n'_v represents a sum over the discrete states and an integral over the continuum that also involves negative energies. The dipole tensor polarizability is defined as [1,9]

$$\alpha_1^T(v) = 4\sqrt{\frac{5j_v(2j_v-1)[j_v]}{6(j_v+1)(2j_v+3)}}\sum_{\kappa'_v}(-1)^{j_v+j'_v}[j'_v]\begin{Bmatrix} j_v & 1 & j'_v \\ 1 & j_v & 2 \end{Bmatrix}\begin{pmatrix} j'_v & 1 & j_v \\ -1/2 & 0 & 1/2 \end{pmatrix}^2 \mathop{\sum\!\!\!\!\!\!\!\int}_{n'_v} \frac{\left\{\int_0^\infty [P_v(r)P_{v'}(r) + Q_v(r)Q_{v'}(r)]\tilde{r}\, dr\right\}^2}{\varepsilon_{v'} - \varepsilon_v}. \tag{15}$$

D. Decay rates and lifetimes

The lifetime (in s) of an atomic state is given by the inverse of the sum of all possible decay rates (in s^{-1}), $\tau = 1/\sum_i W_i$. The dominant one-photon $E2$ and $M1$ and two-photon $2E1$ contributions are studied in this work.

For an atomic system described with Eq. (6), the average partial decay rates describing the $2E1$ two-photon transitions read in a.u. [49,61,63]

$$\frac{d\overline{W}_{2E1}}{d\omega_1} = \frac{\omega_1\omega_2}{8\pi^3c^2[j_i]}\sum_{j_v}\left\{\left[S_{2E1}^{j_v}(2,1)\right]^2 + \left[S_{2E1}^{j_v}(1,2)\right]^2 + 2\sum_{j'_v} d_{2E1}^{j_v,j'_v}\, S_{2E1}^{j_v}(2,1)S_{2E1}^{j'_v}(1,2)\right\}, \tag{16}$$

where the angular coupling factor $d_{2E1}^{j_v,j'_v}$ is given in Ref. [49], and $S_{2E1}^{j_v}(2,1)$ reads

$$S_{2E1}^{j_v}(2,1) = \Delta_{2E1}^{j_v}(2,1)\sum_{\kappa_v}\mathop{\sum\!\!\!\!\!\!\!\int}_{n_v}\frac{\overline{\mathcal{M}}_{f,v}^{E1}(\omega_2;G)\,\overline{\mathcal{M}}_{v,i}^{E1}(\omega_1;G)}{\varepsilon_v - \varepsilon_i + \omega_1}. \tag{17}$$

The angular factor $\Delta^{j_v}_{2E1}(2,1)$ is given in Ref. [49]. $S^{j_v}_{2E1}(1,2)$ is analogously obtained by permuting indices 1 and 2. Kets $|i\rangle \equiv |n_i\kappa_i\rangle$ and $|f\rangle \equiv |n_f\kappa_f\rangle$ correspond to solutions of Eq. (6) for the initial and final states with respective energies ε_i and ε_f, and ω_j is the frequency of the jth photon. Energy conservation imposes $\varepsilon_i - \varepsilon_f = \omega_1 + \omega_2$, where the recoil of the nucleus is neglected. As for polarizabilities, the transition proceeds through an infinite set of intermediate states $|v\rangle \equiv |n_v\kappa_v\rangle$ at energy ε_v.

The electric radial matrix elements $\overline{\mathcal{M}}^{EL}$ in Eq. (17) contain an arbitrary gauge parameter G from which the results should be independent [61,62]. The $G = 0$ value defines the Coulomb (or velocity) gauge, which leads to the electric multipole velocity form in the nonrelativistic limit. The value $G = \sqrt{(L+1)/L}$ defines the Babushkin (or length) gauge, which leads to the nonrelativistic electric multipole length form of the transition operator, and hence allows to account for correction (12).

In the long-wavelength (LW) approximation [39,62], the radial matrix element $\overline{\mathcal{M}}^{E1}_{\alpha,\beta}$ in Eq. (17) reads in the length gauge [62]

$$\overline{\mathcal{M}}^{E1}_{\alpha,\beta}(\omega;\sqrt{2}) = \sqrt{2}\left(\frac{\omega}{c}\right)\int_0^\infty [P_\alpha(r)P_\beta(r) + Q_\alpha(r)Q_\beta(r)]\tilde{r}\,dr. \tag{18}$$

The spontaneous $2E1$ decay rate, W_{2E1}, is obtained by integrating $d\overline{W}_{2E1}/d\omega_1$ over ω_1 from 0 to $\varepsilon_i - \varepsilon_f$. The value of W_{2E1} is multiplied by 1/2 to avoid counting twice each pair, because both photons have the same characteristics [63].

The spontaneous emission rate for a one-photon transition $i \to f$ reads in a.u. [62]

$$W_{i\to f} = \frac{2\omega_t}{c}\frac{[j_f]}{[L]}\begin{pmatrix} j_i & L & j_f \\ 1/2 & 0 & -1/2 \end{pmatrix}^2 |\overline{\mathcal{M}}^{\sigma L}_{fi}(\omega_t)|^2, \tag{19}$$

where $\sigma = E$ or M, and $\omega_t = \varepsilon_i - \varepsilon_f$ is the transition energy. In the LW approximation, $\overline{\mathcal{M}}^{E2}_{fi}$ reads in the length gauge [62]

$$\overline{\mathcal{M}}^{E2}_{fi}(\omega_t;\sqrt{3/2}) = \frac{1}{\sqrt{6}}\left(\frac{\omega_t}{c}\right)^2\int_0^\infty [P_f(r)P_i(r) + Q_f(r)Q_i(r)]\tilde{r}^2\,dr, \tag{20}$$

and the gauge-independent radial matrix element $\overline{\mathcal{M}}^{M1}_{fi}$ is given by [62]

$$\overline{\mathcal{M}}^{M1}_{fi}(\omega_t) = \frac{1}{\sqrt{2}}\left(\frac{\omega_t}{c}\right)(\kappa_f + \kappa_i)\int_0^\infty [P_f(r)Q_i(r) + Q_f(r)P_i(r)]r\,dr. \tag{21}$$

No correction similar to Eq. (12) is applied to the magnetic transition operator. The excellent comparison between the present $M1$ decay rates and the reference values [64] (see Table VII) infers that such corrections would be small.

The use of the LW approximation is justified by the small variation (only on the sixth digit) found in the obtained results when considering $(\omega r/c)^L/(2L+1)!!$ operators instead of spherical Bessel functions $j_L(\omega r/c)$ that occur in the relativistic transition operators [62].

The multipole matrix elements involved in the calculation of polarizabilities, one- and two-photon decay rates are dominated by the form of the wave function at long distances from the nucleus. By tuning energies to experimental values, semiempirical-core-potential methods enable to obtain wave functions having the correct asymptotic decrease [9].

III. LAGRANGE-MESH METHOD

A. Expansions on a Lagrange basis

The principles of the LMM are described in Refs. [44–46], and its application to the Dirac equation is presented in Refs. [45] and [47]. The mesh points x_j are defined by [44]

$$L^\alpha_N(x_j) = 0, \tag{22}$$

where $j = 1$ to N, and L^α_N is a generalized Laguerre polynomial [65]. This mesh is associated with a Gauss-Laguerre quadrature

$$\int_0^\infty g(x)\,dx \approx \sum_{j=1}^N \lambda_j\, g(x_j), \tag{23}$$

with the weights λ_j. Note that the dependence of x_j and λ_j on parameter α is implicit. The Gauss quadrature is exact for the Laguerre weight function $x^\alpha e^{-x}$ multiplied by any polynomial of degree at most $2N-1$ [66]. The regularized Lagrange functions are defined by [45,67,68]

$$\hat{f}^{(\alpha)}_j(x) = (-1)^j\sqrt{\frac{N!}{\Gamma(N+\alpha+1)x_j}}\,\frac{L^\alpha_N(x)}{x-x_j}\,x^{\alpha/2+1}e^{-x/2}. \tag{24}$$

The functions $\hat{f}^{(\alpha)}_j(x)$ are polynomials of degree $N-1$ multiplied by x and by the square root of the Laguerre weight $x^\alpha e^{-x}$. The Lagrange functions satisfy the Lagrange conditions

$$\hat{f}^{(\alpha)}_j(x_i) = \lambda_i^{-1/2}\delta_{ij}. \tag{25}$$

They are not orthonormal, but become orthonormal at the Gauss-quadrature approximation. Condition (25) drastically simplifies the expressions of the one-body matrix elements calculated with the Gauss quadrature.

Radial functions $P_v(r)$ and $Q_v(r)$ are expanded in regularized Lagrange functions (24) as

$$P_v(r) = h_v^{-1/2}\sum_{j=1}^{N_v} p_{vj}\,\hat{f}^{(\alpha)}_j(r/h), \tag{26}$$

$$Q_v(r) = h_v^{-1/2}\sum_{j=1}^{N_v} q_{vj}\,\hat{f}^{(\alpha)}_j(r/h), \tag{27}$$

where h_v is a scaling parameter aimed at adapting the scaled mesh $\{h_v x_i\}_{i=1}^{N_v}$ to the physical extension of the problem. The parameter $\alpha_v = 2(\gamma_v - 1)$, where $\gamma_v = \sqrt{\kappa_v^2 - (\alpha Z)^2}$, can be selected so that the Lagrange functions behave as r^{γ_v} near the origin [47]. Here, another choice $\alpha_v = 2(\gamma_v - |\kappa_v|)$ is preferable [48,49]. The basis functions then behave as $r^{\gamma_v - |\kappa_v| + 1}$, and the physical r^{γ_v} behavior can be simulated by linear combinations.

Let us introduce expansions (26) and (27) in Eq. (6). Projecting on the Lagrange functions and using the associated Gauss quadrature leads to the $2N_v \times 2N_v$ Hamiltonian matrix,

$$\boldsymbol{H}^{\mathrm{DHFCP}}_{\kappa_v} = \boldsymbol{H}_{\kappa_v} + \begin{pmatrix} V^{\mathrm{pp}}_{\mathrm{dir}} & 0 \\ 0 & V^{\mathrm{qq}}_{\mathrm{dir}} \end{pmatrix} + \begin{pmatrix} V^{\mathrm{pp}}_{\mathrm{exc}} & V^{\mathrm{pq}}_{\mathrm{exc}} \\ V^{\mathrm{qp}}_{\mathrm{exc}} & V^{\mathrm{qq}}_{\mathrm{exc}} \end{pmatrix} + \begin{pmatrix} V^{\mathrm{pp}}_{\mathrm{CP}} & 0 \\ 0 & V^{\mathrm{qq}}_{\mathrm{CP}} \end{pmatrix}, \tag{28}$$

where the $N_v \times N_v$ block matrices verify $V^{\mathrm{pp}}_{\mathrm{dir}} = V^{\mathrm{qq}}_{\mathrm{dir}}$, $V^{\mathrm{qp}}_{\mathrm{exc}} = (V^{\mathrm{pq}}_{\mathrm{exc}})^T$, and $V^{\mathrm{pp}}_{\mathrm{CP}}(i,j) = V^{\mathrm{qq}}_{\mathrm{CP}}(i,j) = V_{\mathrm{CP}}(h_v x_i)\,\delta_{ij}$. The matrix $\boldsymbol{H}_{\kappa_v}$ corresponds to the $2N_v \times 2N_v$ hydrogenlike Dirac Hamiltonian at the Gauss-quadrature approximation, and reads

$$\boldsymbol{H}_{\kappa_v} = \begin{pmatrix} -Z/(h_v x_i)\,\delta_{ij} & \frac{c}{h_v}\left(D^G_{ji} + \frac{\kappa_v}{x_i}\delta_{ij}\right) \\ \frac{c}{h_v}\left(D^G_{ij} + \frac{\kappa_v}{x_i}\delta_{ij}\right) & [-Z/(h_v x_i) - 2c^2]\,\delta_{ij} \end{pmatrix}, \tag{29}$$

with a 2×2 block structure, where the matrix elements $D_{ij} = \langle \hat{f}^{(\alpha_v)}_i | d/dx | \hat{f}^{(\alpha_v)}_j \rangle$ are calculated at the Gauss-quadrature approximation as

$$D^G_{i\neq j} = (-1)^{i-j}\sqrt{\frac{x_i}{x_j}}\,\frac{1}{x_i - x_j}, \quad D^G_{ii} = \frac{1}{2x_i}. \tag{30}$$

The diagonalization of Hamiltonian matrix (28) provides a set of $2N_v$ orthogonal eigenvectors $\boldsymbol{p}_v = (p_{v1},\ldots,p_{vN_v},q_{v1},\ldots,q_{vN_v})^T$ for each valence orbital ϕ_v of a given κ_v symmetry, and $\sum_{j=1}^{N_v}(p^2_{vj} + q^2_{vj}) = 1$ ensures the normalization of $P_v(r)$ and $Q_v(r)$ at the Gauss-quadrature approximation.

B. Evaluation of two-electron Slater integrals

Let us illustrate the calculation of the two-electron Slater integrals R^k by considering, e.g., the exchange potential matrix in Eq. (28). The matrix element (i,j) of the $N_v \times N_v$ block $V^{\mathrm{pq}}_{\mathrm{exc}}$ is given by Eq. (10), where the integral $R^k_{\mathrm{pq}}(ic,cj)$ reads, according to Eq. (5),

$$R^k_{\mathrm{pq}}(ic,cj) = h_v^{-1}\int_0^\infty\int_0^\infty \hat{f}^{(\alpha_v)}_i(r_1/h_v)P_c(r_1) \times \frac{r^k_<}{r^{k+1}_>}\,Q_c(r_2)\hat{f}^{(\alpha_v)}_j(r_2/h_v)\,dr_1 dr_2. \tag{31}$$

Two integration methods are devised in order to accurately compute $R^k_{\mathrm{pq}}(ic,cj)$ with Gauss-Laguerre quadratures. The first one, denoted as "M I", corresponds to the strategy suggested by Hartree [41,69], who first introduced the functions $Y^k(bd;r)$. In the present case (31), $Y^k_q(jc;r)$ reads

$$Y^k_q(jc;r) = r\int_0^\infty \frac{r^k_<}{r^{k+1}_>}\,Q_c(s)h_v^{-1/2}\hat{f}^{(\alpha_v)}_j(s/h_v)\,ds, \tag{32}$$

with $r \equiv r_1$ and $s \equiv r_2$, and is the solution of the second-order differential equation

$$\frac{d^2}{dr^2}\,Y^k_q(jc;r) - \frac{k(k+1)}{r^2}\,Y^k_q(jc;r) = -\frac{2k+1}{r}\,Q_c(r)h_v^{-1/2}\hat{f}^{(\alpha_v)}_j(r/h_v) \tag{33}$$

with the boundary conditions $Y^k_q(jc;0) = 0$ and $dY^k_q(jc;r)/dr \to -kY^k_q(jc;r)/r + Q_c(r)h_v^{-1/2}\ \hat{f}^{(\alpha_v)}_j(r/h_v)$ as $r \to \infty$. Special attention is required for the $k = 0$ case for which $Y^0_q(jc;\infty) = \int_0^\infty Q_c(s)h_v^{-1/2}\hat{f}^{(\alpha_v)}_j(s/h_v)\,ds$, whereas $Y^k_q(jc;\infty) = 0$ for $k > 0$. Equation (33) is solved on Lagrange meshes, as presented in the Appendix. Once $Y^k_q(jc;r)$ is known, the two-electron Slater integral (31) is expressed as

$$R^k_{\mathrm{pq}}(ic,cj) = \int_0^\infty h_v^{-1/2}\hat{f}^{(\alpha_v)}_i(r/h_v)P_c(r)\,\frac{1}{r}\,Y^k_q(jc;r)\,dr \tag{34}$$

and can be computed with the appropriate Gauss-Laguerre quadrature (see the Appendix).

The second method, denoted as "M II", separates $R^k_{\mathrm{pq}}(ic,cj)$ in two terms as

$$R^k_{\mathrm{pq}}(ic,cj) = h_v^{-1}\int_0^\infty \hat{f}^{(\alpha_v)}_j(r_2/h_v)Q_c(r_2)\,r_2^k\int_{r_2}^\infty \frac{\hat{f}^{(\alpha_v)}_i(r_1/h_v)P_c(r_1)}{r_1^{k+1}}\,dr_1 dr_2 + h_v^{-1}\int_0^\infty \frac{\hat{f}^{(\alpha_v)}_j(r_2/h_v)Q_c(r_2)}{r_2^{k+1}}\int_0^{r_2}\hat{f}^{(\alpha_v)}_i(r_1/h_v)P_c(r_1)\,r_1^k\,dr_1 dr_2. \tag{35}$$

The first term is denoted as $\mathcal{R}^k_{\mathrm{pq}}(ic,cj)$, and the order of integration is permuted in the second term. The integration bounds $r_1 \in [0,r_2]$ and $r_2 \in [0,\infty[$ become $r_1 \in [0,\infty[$ and $r_2 \in [r_1,\infty[$, leading to

$$R^k_{\mathrm{pq}}(ic,cj) = \mathcal{R}^k_{\mathrm{pq}}(ic,cj) + \mathcal{R}^k_{\mathrm{qp}}(jc,ci). \tag{36}$$

By using the change of variable $r_1 = r + r_2$, $\mathcal{R}^k_{\mathrm{pq}}(ic,cj)$ is integrated over variables r_2 and r, and reads

$$\mathcal{R}^k_{\mathrm{pq}}(ic,cj) = h_v^{-1}\int_0^\infty \hat{f}^{(\alpha_v)}_j(r_2/h_v)Q_c(r_2)\,r_2^k\int_0^\infty \frac{\hat{f}^{(\alpha_v)}_i[(r+r_2)/h_v]P_c(r+r_2)}{(r+r_2)^{k+1}}\,dr dr_2. \tag{37}$$

This double integral is evaluated with two different Gauss-Laguerre quadratures, one for each integration variable (see the Appendix). Gauss quadratures of $R^k_{\mathrm{pp}}(ic,cj)$ and $R^k_{\mathrm{qq}}(ic,cj)$ are analogously obtained using M I and M II, as well as the Slater integral $R^0_{\mathrm{pp}}(ic,jc)$ involved in the $N_v \times N_v$ block $V^{\mathrm{pp}}_{\mathrm{dir}}$ of Eq. (28).

C. Projection of core orbitals on Lagrange bases

Each GRASP2K core orbital is expanded over a basis of Lagrange functions depending on the parameter $\alpha_c = 2(\gamma_c - |\kappa_c|)$. A different value of h_c is assigned to each orbital and is chosen such that the largest GRASP2K grid point of orbital c, R_c, is at the center of $[h_c x_{N_c-1}, h_c x_{N_c}]$, where x_{N_c-1} and x_{N_c} denote the last two Lagrange mesh points, i.e., $h_c = 2R_c/(x_{N_c-1} + x_{N_c})$. To compute the unknown $\{p_{cj}\}_{j=1}^{N_c}$ and $\{q_{cj}\}_{j=1}^{N_c}$ coefficients for each core orbital, the radial wave functions $P_c(r)$ and $Q_c(r)$ are evaluated at each point $h_c x_i$ of the scaled Lagrange mesh. Because the GRASP2K grid points do not correspond to Lagrange mesh points, the wave functions are first interpolated with cubic splines, which are piecewise polynomials, allowing to evaluate the functions at any r. Applying the Lagrange condition (25) respectively yields the expansion coefficients $p_{ci} = (h_c\lambda_i)^{1/2}\, P_c(h_c x_i)$ and $q_{ci} = (h_c\lambda_i)^{1/2}\, Q_c(h_c x_i)$, for $i = 1$ to N_c.

D. Polarizabilities and decay rates on Lagrange meshes

Polarizabilities and two-photon decay rates proceed through an infinite set of intermediate states with some value of κ'_ν. Finite-basis techniques such as the LMM allow a discretization of the continuum, leading to a truncated sum over $2N'_\nu$ intermediate states. Some of these states may correspond to approximate eigenstates of Eq. (6), while the other ones, discretizing the continuum, have no physical meaning and are called *pseudostates*.

Let $\varepsilon_{n'_\nu\kappa'_\nu}$, $n'_\nu = 1,\ldots,2N'_\nu$ be the eigenvalues of matrix $\boldsymbol{H}^{\mathrm{DHFCP}}_{\kappa'_\nu}$ with κ'_ν replacing κ_ν. The corresponding eigenvectors contain the coefficients $p_{\nu' j}$ and $q_{\nu' j}$ of the components $P_{\nu'}(r)$ and $Q_{\nu'}(r)$ of the intermediate states. The latter are calculated with $\alpha'_\nu = 2(\gamma'_\nu - |\kappa'_\nu|)$ in place of $\alpha_\nu = 2(\gamma_\nu - |\kappa_\nu|)$, i.e., matrix $\boldsymbol{H}^{\mathrm{DHFCP}}_{\kappa'_\nu}$ is calculated on a different mesh $h'_\nu x'_j$ with N'_ν mesh points. Hence, the physical intermediate states have the exact behavior $r^{\gamma'_\nu}$ at the origin. Accurate calculations of Eqs. (14), (15), and (17) with a Gauss-Laguerre quadrature are possible by choosing a third mesh $\bar{h}\bar{x}_i$ where $\bar{h} = 2h_\nu h'_\nu/(h_\nu + h'_\nu)$. In the two-photon case, h_ν corresponds to h_i or h_f. The $\bar{x}_i$ correspond to the weight function $x^{\bar{\alpha}}e^{-x}$ with $\bar{\alpha} = (\alpha_\nu + \alpha'_\nu)/2$, and the corresponding weights are denoted as $\bar{\lambda}_i$.

Approximate scalar polarizabilities $\alpha^S_\lambda(\nu)$ are obtained from Eq. (14) as

$$\alpha^S_\lambda(\nu) = \sum_{\kappa'_\nu} \frac{2[j'_\nu]}{[\lambda]} \begin{pmatrix} j'_\nu & \lambda & j_\nu \\ -1/2 & 0 & 1/2 \end{pmatrix}^2 \times \sum_{n'_\nu=1}^{2N'_\nu} \frac{\left\{\int_0^\infty [P_\nu(r)P_{\nu'}(r) + Q_\nu(r)Q_{\nu'}(r)]\tilde{r}^\lambda\, dr\right\}^2}{\varepsilon_{\nu'} - \varepsilon_\nu}. \tag{38}$$

Tensor polarizabilities $\alpha^T_1(\nu)$ are analogously approximated from Eq. (15).

Similarly, approximate $S^{j'}_{2E1}(2,1)$ terms of the $2E1$ decay rates (16) are obtained from Eq. (17) as

$$S^{j'}_{2E1}(2,1) = \Delta^{j'}_{2E1}(2,1) \sum_{\kappa'} \sum_{n'=1}^{2N'} \frac{\overline{\mathcal{M}}^{E1}_{f,n'\kappa'}(\omega_2;G)\, \overline{\mathcal{M}}^{E1}_{n'\kappa',i}(\omega_1;G)}{\varepsilon_{n'\kappa'} - \varepsilon_i + \omega_1}, \tag{39}$$

where the notations n_ν, j_ν, and κ_ν related to the intermediate states ν are replaced by n', j', and κ'. $S^{j'}_{2E1}(1,2)$ are analogously approximated. The integral common to Eqs. (38) and (39) is calculated with the Gauss quadrature as

$$\int_0^\infty [P_{n\kappa}(r)P_{n'\kappa'}(r) + Q_{n\kappa}(r)Q_{n'\kappa'}(r)]\tilde{r}^k\, dr \approx \sum_{j=1}^{N} \sum_{j'=1}^{N'} [p_{n\kappa j}\, p_{n'\kappa' j'} + q_{n\kappa j}\, q_{n'\kappa' j'}]\, \mathcal{I}^k_{jj'}, \tag{40}$$

where $\mathcal{I}^k_{jj'}$ reads

$$\mathcal{I}^k_{jj'} = \int_0^\infty h^{-1/2}\, \hat{f}^{(\alpha)}_j(r/h)\, \tilde{r}^k\, h'^{-1/2}\, \hat{f}^{(\alpha')}_{j'}(r/h')\, dr \approx \bar{h}(hh')^{-1/2} \sum_{i=1}^{N_G} \bar{\lambda}_i\, \hat{f}^{(\alpha)}_j(\bar{h}\bar{x}_i/h)\, \tilde{r}^k(\bar{x}_i)\, \hat{f}^{(\alpha')}_{j'}(\bar{h}\bar{x}_i/h'), \tag{41}$$

and the nonpolynomial factor $\tilde{r}^k(\bar{x}_i)$ is given by

$$\tilde{r}^k(\bar{x}_i) = (\bar{h}\bar{x}_i)^k - \frac{\alpha_k(\mathrm{core})}{(\bar{h}\bar{x}_i)^{k+1}} \sqrt{1 - \exp[-(\bar{h}\bar{x}_i)^{2(k+2)}/\bar{\rho}^{2(k+2)}]}. \tag{42}$$

If $\tilde{r}^k$ was replaced by r^k, the Gauss quadrature (23) would be exact with $N_G \geqslant (N + N' + k + 1)/2$ mesh points. This suggests the use of $N_G > (N + N' + k + 1)/2$ in the present case. The integrals appearing in the one-photon $E2$ and $M1$ decay rates (20) and (21) are analogously calculated with a Gauss-Laguerre quadrature.

In the two-photon case, the integral over ω_1 is evaluated with a Gauss-Legendre quadrature using N_{ω_1} mesh points.

IV. NUMERICAL RESULTS

A. Calculations of core orbitals

The core orbitals of each ion are calculated with GRASP2K and are projected on Lagrange bases. Comparing the original orbitals, the one- and two-electron integrals, and the core energies with those computed with the LMM allows one to assess the accuracy of the core description within the present approach.

Let us first compute with the LMM the norm, mean values of powers of r, and core-orbital overlaps and compare them with the GRASP2K results. Any orbital from GRASP2K being orthonormal, the error on the norm can be written as $\sqrt{\langle\phi_{n_c\kappa_c}|\phi_{n_c\kappa_c}\rangle} - 1$, where $\langle\phi_{n_c\kappa_c}|\phi_{n_c\kappa_c}\rangle \approx \sum_{j=1}^{N_c} (p^2_{n_c\kappa_c j} + q^2_{n_c\kappa_c j})$ at the Gauss-quadrature approximation. Similarly, mean values of powers of r read $\langle r^s\rangle_{n_c\kappa_c} \approx \sum_{j=1}^{N_c} (h_c x_j)^s (p^2_{n_c\kappa_c j} + q^2_{n_c\kappa_c j})$ with the Gauss quadrature,

TABLE I. Contribution of one- (I_{tot}) and two-electron (R_{tot}) terms to Ca^{2+}, Sr^{2+}, and Ba^{2+} core energies, E_{core} (in a.u.). LMM M I and M II values are compared with GRASP2K results. Powers of 10 are indicated within brackets.

Term	M I	M II	GRASP2K
		Ca^{2+}	
I_{tot}	−9.197 475 6 [2]		−9.197 470 37 [2]
R_{tot}	2.406 424 7 [2]	2.406 422 8 [2]	2.406 419 74 [2]
E_{core}	−6.791 050 9 [2]	−6.791 052 8 [2]	−6.791 050 63 [2]
		Sr^{2+}	
I_{tot}	−4.378 474 7 [3]		−4.378 471 73 [3]
R_{tot}	1.200 919 8 [3]	1.200 919 5 [3]	1.200 917 63 [3]
E_{core}	−3.177 554 9 [3]	−3.177 555 2 [3]	−3.177 554 10 [3]
		Ba^{2+}	
I_{tot}	−1.107 863 7 [4]		−1.107 862 86 [4]
R_{tot}	2.943 151 2 [3]	2.943 151 1 [3]	2.943 145 62 [3]
E_{core}	−8.135 485 8 [3]	−8.135 485 9 [3]	−8.135 482 95 [3]

which is exact for $s = -2$ and -1. The exactness for $s \geqslant 0$ is recovered by choosing $N_G \geqslant (2N_c + s + 1)/2$ mesh points. The overlap $\langle \phi_{n_c\kappa_c} | \phi_{n'_c\kappa_c} \rangle$ within the same κ_c symmetry is given by Eqs. (40) and (41) with $\kappa = \kappa' = \kappa_c$ and $k = 0$. Using a basis of $N_c = 50$ Lagrange functions for Ca^{2+}, Sr^{2+}, and Ba^{2+}, all relative errors with respect to GRASP2K are in the range $10^{-7} - 10^{-6}$.

Let us now compute with the LMM the core energies (3), E_{core}, and compare them with the GRASP2K results. Projecting $P_c(r)$ and $Q_c(r)$ on N_c Lagrange functions and using the Gauss quadrature yields $I(c,c) = \boldsymbol{p}_c^T \boldsymbol{H}_{\kappa_c} \boldsymbol{p}_c$ for the one-electron integrals (4), where $\boldsymbol{p}_c = (p_{c1},\ldots,p_{cN_c},q_{c1},\ldots,q_{cN_c})^T$, and the $2N_c \times 2N_c$ matrix $\boldsymbol{H}_{\kappa_c}$ is given by Eq. (29) with κ_c instead of κ_v. According to Eq. (3), the total one-electron energy of the core is expressed as $I_{\text{tot}} = \sum_c q_c\, I(c,c)$. The two-electron Slater integrals (5) are computed using methods M I and M II. The Appendix provides expressions on Lagrange meshes for the valence case. Similar expressions can be derived for the Slater integrals $R^k(cc,cc)$, $R^0(cc',cc')$, and $R^k(cc',c'c)$. The total two-electron energy of the core, R_{tot}, is expressed as $E_{\text{core}} - I_{\text{tot}}$, i.e., as the sum of the last two terms on the right-hand side of Eq. (3).

Table I displays the Ca^{2+}, Sr^{2+}, and Ba^{2+} core energies using a basis of $N_c = 50$ Lagrange functions. The relative error on I_{tot} with respect to GRASP2K ranges from 5.7×10^{-7} to 7.4×10^{-7}. Hence, the accuracy on one-electron integrals is of the same order of magnitude as the one on the wave functions themselves. The relative error on R_{tot} is 2×10^{-6}, and both M I and M II provide the same order of accuracy. Summing the one- and two-electron contributions, the accuracy on E_{core} is 3×10^{-7} for M I and M II. Increasing the number of Lagrange functions beyond $N_c = 50$ does not improve the accuracy of the results.

TABLE II. DHF and DHFCP energies, $\varepsilon_v^{\text{DHF}}$ and $\varepsilon_v^{\text{DHFCP}}$ (in a.u.), of the five lowest states in Ca^+, Sr^+, and Ba^+. Energies are given relative to the energy of the core. DHF-LMM values are compared with results from GRASP2K.

	$\varepsilon_v^{\text{DHF}}$		$\varepsilon_v^{\text{DHFCP}}$
State	LMM	GRASP2K	LMM
		Ca^+	
$4s_{1/2}$	−0.416 626	−0.416 631 56	−0.436 277 6
$3d_{3/2}$	−0.330 859	−0.330 869 35	−0.374 082 8
$3d_{5/2}$	−0.330 750	−0.330 759 53	−0.373 806 3
$4p_{1/2}$	−0.309 994	−0.309 998 55	−0.321 496 7
$4p_{3/2}$	−0.309 084	−0.309 088 86	−0.320 481 1
		Sr^+	
$5s_{1/2}$	−0.382 915	−0.382 927 55	−0.405 355 2
$4d_{3/2}$	−0.307 011	−0.307 028 86	−0.339 033 6
$4d_{5/2}$	−0.306 360	−0.306 378 05	−0.337 756 3
$5p_{1/2}$	−0.284 816	−0.284 826 03	−0.297 300 8
$5p_{3/2}$	−0.281 698	−0.281 707 26	−0.293 649 1
		Ba^+	
$6s_{1/2}$	−0.343 264	−0.343 286 19	−0.367 633 8
$5d_{3/2}$	−0.310 428	−0.310 459 81	−0.345 426 9
$5d_{5/2}$	−0.308 268	−0.308 299 53	−0.341 777 5
$6p_{1/2}$	−0.260 904	−0.260 920 58	−0.275 315 4
$6p_{3/2}$	−0.254 560	−0.254 576 95	−0.267 611 3

B. Calculations of valence orbitals

Table II displays DHF and DHFCP energies, $\varepsilon_v^{\text{DHF}}$ and $\varepsilon_v^{\text{DHFCP}}$ (in a.u.), of the five lowest states in Ca^+, Sr^+, and Ba^+ ions, relative to the core energy. The results are computed with $N_c = N_v = 50$ Lagrange functions. The values of the scaling parameter h_v are 0.10 for nd_j states, 0.11 for $(n+1)s_{1/2}$ states, and 0.12 for $(n+1)p_j$ states. In practice, all values between 0.1 and 0.2 are acceptable for these states.

DHF-LMM values, obtained by neglecting $V_{\text{CP}}(r)$ in Eq. (8), are compared with results from GRASP2K at the frozen-core approximation. The relative error on $\varepsilon_v^{\text{DHF}}$ with respect to GRASP2K is similar for M I and M II, and slightly increases with Z, ranging from 1.4×10^{-5} to 3.3×10^{-5} in Ca^+, from 3.3×10^{-5} to 5.9×10^{-5} in Sr^+, and from 6.3×10^{-5} to 9.9×10^{-5} in Ba^+. Besides, the fine-structure splittings are well reproduced for the nd_j and $(n+1)p_j$ states. The accuracy of the present valence calculations is sufficient to obtain reliable results for polarizabilities, one- and two- photon decay rates, and associated lifetimes when adding the contribution of $V_{\text{CP}}(r)$, as shown in Secs. IV C and IV D. Increasing the number of Lagrange functions beyond $N_v = 50$ does not improve the accuracy of the results.

The values of the core static dipole polarizabilities used in the DHFCP-LMM calculations are computed at the relativistic random-phase approximation (RRPA) and are taken from Ref. [71]: $\alpha_1(\text{Ca}^{2+}) = 3.254$ a.u., $\alpha_1(\text{Sr}^{2+}) = 5.813$ a.u., and $\alpha_1(\text{Ba}^{2+}) = 10.61$ a.u. The ρ_{κ_v} values (in a.u.), listed in Table III, ensure that the relative error on $\varepsilon_v^{\text{DHFCP}}$ with respect to experimental NIST data [70] is below 10^{-7} for all states presented in Table II, considering both M I and M II. The obtained ρ_{κ_v} numbers show good agreement with the ones provided by Ref. [4] for Ca^+ and by Ref. [9] for Sr^+.

C. Calculations of polarizabilities

Tables IV and V respectively display static scalar dipole (α_1^S) and quadrupole (α_2^S) polarizabilities (in a.u.) of the five

TABLE III. Cutoff parameters, ρ_{κ_v} (in a.u.), for different κ_v symmetries in Ca^+, Sr^+, and Ba^+. Comparison with Refs. [4] and [9].

	ρ_{κ_v} (a.u.)				
	Ca^+		Sr^+		Ba^+
κ_v	LMM	Ref. [4]	LMM	Ref. [9]	LMM
−1	1.73808	1.7419	2.02900	2.04960	2.35081
+1	1.63549	1.6389	1.94914	1.97169	2.24066
−2	1.63216	1.6354	1.95229	1.97600	2.26242
+2	1.84605	1.8472	2.34998	2.35353	2.75043
−3	1.84776	1.8489	2.36151	2.36534	2.77960

lowest states in Ca^+, Sr^+, and Ba^+ ions. Tensor dipole (α_1^T) polarizabilities (in a.u.) are given for the $j_v > 1/2$ states. Core dipole and quadrupole polarizabilities from Ref. [71] are added to the valence scalar values, $\alpha_1^S(v)$ and $\alpha_2^S(v)$. The core quadrupole values are $\alpha_2(Ca^{2+}) = 6.936$ a.u., $\alpha_2(Sr^{2+}) = 17.15$ a.u., and $\alpha_2(Ba^{2+}) = 45.96$ a.u.

The DHFCP-LMM results are computed with $N_c = N_v = N' = 50$ Lagrange functions, where N' denotes the number of functions used to describe the intermediate states. Significant digits are estimated by increasing N' from 50 to 80. The LMM calculations are performed with M I and M II, and the comparison of their results allows one to assess the precision of the values displayed in Tables IV and V.

A more stringent estimate of the precision achieved by the DHFCP-LMM approach is given by studying the effect of variations in the values of the core dipole and quadrupole polarizabilities on the final results. A second set of core dipole values is provided by Ref. [72]: $\alpha_1(Ca^{2+}) = 3.284$ a.u., $\alpha_1(Sr^{2+}) = 5.748$ a.u., and $\alpha_1(Ba^{2+}) = 10.426$ a.u. The relative differences with respect to the first set of values are respectively 0.9%, 1.1%, and 1.7%. A second set of core quadrupole values is provided by Ref. [14] for Ca^{2+} and Sr^{2+}, and by Ref. [11] for Ba^{2+}: $\alpha_2(Ca^{2+}) = 6.15$ a.u., $\alpha_2(Sr^{2+}) = 14.50$ a.u., and $\alpha_2(Ba^{2+}) = 44$ a.u. The relative differences with respect to the first set of values are respectively 11.3%, 15.5%, and 4.3%, thus substantially higher than for the core dipole values.

TABLE IV. Static scalar dipole (α_1^S) polarizabilities (in a.u.) of the five lowest states in Ca^+, Sr^+, and Ba^+. Tensor dipole (α_1^T) polarizabilities (in a.u.) are given for the $j_v > 1/2$ states. Core polarizabilities from Refs. [71,72] are added to the DHFCP-LMM valence $\alpha_1^S(v)$ results. Comparison with other theory and experiment. Uncertainties in the last digits are given within parentheses.

			Ca^+					
	$4s_{1/2}$	$3d_{3/2}$		$3d_{5/2}$		$4p_{1/2}$	$4p_{3/2}$	
Method	α_1^S	α_1^S	α_1^T	α_1^S	α_1^T	α_1^S	α_1^S	α_1^T
DHFCP-LMM	75.272(24)	32.986(10)	−17.884(18)	32.814(10)	−25.174(26)	−3.408(78)	−1.584(77)	10.202(20)
RCICP [3]	75.46(72)	32.98(24)	−17.97(17)	32.80(24)	−25.28(24)	−2.98(11)	−1.12(10)	10.20(11)
DFCP [4]	75.28	32.99	−17.88	32.81	−25.16	−2.774	−0.931	10.12
RMBPT-SD [5]	76.1(5)	32.0(3)	−17.43(23)	31.8(3)	−24.51(29)	−0.75(70)	1.02(64)	10.31(28)
RCCSD [6]	76.03	32.3	−17.02	32.05	−23.92	0.82	2.82	10.08
RCCSD(T) [7]	76.1(2)	33.67(180)	−17.71	33.11(180)	−24.78(4)			
RLCCSD(T) [8]	76.1(11)			32.0(11)				
Expt. SA [73]	75.3(4)							
			Sr^+					
	$5s_{1/2}$	$4d_{3/2}$		$4d_{5/2}$		$5p_{1/2}$	$5p_{3/2}$	
	α_1^S	α_1^S	α_1^T	α_1^S	α_1^T	α_1^S	α_1^S	α_1^T
DHFCP-LMM	89.708(36)	63.102(14)	−35.072(58)	61.979(10)	−47.325(76)	−31.69(21)	−21.43(20)	9.802(41)
RCICP [9]	90.10(127)	63.12(82)	−35.11(50)	61.99(72)	−47.38(67)	−31.29(49)	−20.92(70)	9.836(147)
RMBPT-SD [12]	92.2(7)	63.3(9)	−35.5(6)	62.0(9)	−47.7(8)	−32.2(9)	−21.4(8)	10.74(23)
RCCSD [6]	90.54	63.74	−35.26	62.08	−47.35	−31.27	−20.79	10.52
RCCSD(T) [7]	91.23(30)	64.7(25)	−35.88(5)	63.5(25)	−48.29(7)			
RCCSD(T) [13]	88.29(100)	61.43(52)	−35.42(25)	62.87(75)	−48.83(30)			
RLCCSD(T) [10]	91.3(9)			62.0(5)				
Expt. DFI [74]	86(11)							
			Ba^+					
	$6s_{1/2}$	$5d_{3/2}$		$5d_{5/2}$		$6p_{1/2}$	$6p_{3/2}$	
	α_1^S	α_1^S	α_1^T	α_1^S	α_1^T	α_1^S	α_1^S	α_1^T
DHFCP-LMM	120.74(9)	49.438(26)	−21.403(93)	49.832(28)	−29.183(120)	22.39(41)	45.86(36)	3.110(86)
RCCSD [6]	123.18	53.80	−22.92	56.53	−31.83	20.46	45.53	4.70
RCCSD(T) [7]	123.7(5)	54.17(250)	−22.19(4)	56.87(240)	−32.17(3)			
RCCSD(T) [13]	124.26(100)	48.81(46)	−24.62(28)	50.67(58)	−30.85(31)			
RLCCSD(T) [11]	124.15							
Expt. RESIS [75]	123.88(5)							

TABLE V. Static scalar quadrupole (α_2^S) polarizabilities (in a.u.) of the five lowest states in Ca^+, Sr^+, and Ba^+. Core polarizabilities from Refs. [11,14,71] are added to the DHFCP-LMM valence $\alpha_2^S(v)$ results. Comparison with other theory and experiment. Uncertainties in the last digits are given within parentheses.

			Ca^+		
Method	$4s_{1/2}$ α_2^S	$3d_{3/2}$ α_2^S	$3d_{5/2}$ α_2^S	$4p_{1/2}$ α_2^S	$4p_{3/2}$ α_2^S
DHFCP-LMM	875.78(223)	5143(111)	−3435(76)	74803(150)	−35781(76)
DFCP [4]	882.43	4928	−3304	74660	−35710
RCCSD(T) [14]	906(5)		−3706(75)		
RMBPT-SD [5]	871(4)				
			Sr^+		
	$5s_{1/2}$ α_2^S	$4d_{3/2}$ α_2^S	$4d_{5/2}$ α_2^S	$5p_{1/2}$ α_2^S	$5p_{3/2}$ α_2^S
DHFCP-LMM	1351.7(44)	2777(43)	−1773(36)	31576(79)	−13091(43)
RCICP [9]	1356.3(315)	2713(44)	−1728(23)	31596(455)	−13099(225)
RCCSD(T) [14]	1366(9)		−1732(41)		
RMBPT-SD [12]	1370.0(28)				
Expt. DFI [74]	$1.1(10)\times10^3$				
			Ba^+		
	$6s_{1/2}$ α_2^S	$5d_{3/2}$ α_2^S	$5d_{5/2}$ α_2^S	$6p_{1/2}$ α_2^S	$6p_{3/2}$ α_2^S
DHFCP-LMM	4067(4)	728.4(15)	−1127(6)	23423(4)	−6973(7)
RLCCSD(T) [11]	4182(34)				
Expt. RESIS [75]	4420(250)				

Using the second set of core polarizabilities in Eqs. (11) and (12) enables estimation of theoretical uncertainties on the values displayed in Tables IV and V. Note that using another set of core dipole values implies determination of other ρ_{κ_v} values in Eq. (11) to ensure relative errors on $\varepsilon_v^{\mathrm{DHFCP}}$ below 10^{-7} with respect to NIST data.

In order to study the accuracy of the DHFCP-LMM approach, the present results are compared with other semiempirical-core-potential approaches (RCICP–relativistic configuration interaction with a semiempirical core potential, DFCP–Dirac-Fock with a semiempirical core potential), with *ab initio* methods (RMBPT-SD–relativistic many-body perturbation theory with single and double contributions, R(L)CCSD(T)–relativistic (linearized) coupled cluster method with single, double (and partial triple) contributions), and with experimental works (SA–spectral analysis, DFI–delayed field ionization, RESIS–resonant excitation Stark ionization spectroscopy).

1. Dipole polarizabilities

The ground $(n+1)s_{1/2}$ dipole polarizabilities involve $n'p_{1/2,3/2}$ intermediate states. They are dominated by the resonant $(n+1)s_{1/2} \rightarrow (n+1)p_j$ transitions, and their accuracy is largely dependent on the accuracy of the transition matrix elements connecting these states. Excellent consistency is found with RCICP [3] and DFCP [4] for Ca^+ $(n=3)$ and with RCICP [9] for Sr^+ $(n=4)$, while no reference value is available with these approaches for Ba^+ $(n=5)$. The agreement with *ab initio* calculations is satisfactory, although the present method tends to underestimate α_1^S by a few percents. This is also true for the RCICP and DFCP methods, and is a direct consequence of the slightly different line strengths for the resonant transitions in these two types of calculations. Good agreement with observation is found for Ca^+, while the large uncertainty of the experimental value for Sr^+ cannot be used to discriminate between theoretical estimates. By contrast, *ab initio* calculations are more consistent with experiment than the present one for Ba^+.

The nd_j dipole polarizabilities involve $n'p_{1/2,3/2}$,$n'f_{5/2}$ states for $nd_{3/2}$, and $n'p_{3/2}$,$n'f_{5/2,7/2}$ states for $nd_{5/2}$. The results of α_1^S and α_1^T are consistent with RCICP and DFCP for Ca^+ and Sr^+. The agreement with *ab initio* methods is satisfactory for Ca^+ and Sr^+, while for Ba^+ better agreement is found with Ref. [13] than with Refs. [6] and [7].

The $(n+1)p_j$ dipole polarizabilities involve $n's_{1/2}$,$n'd_{3/2}$ states, and additional $n'd_{5/2}$ states for $(n+1)p_{3/2}$. Negative α_1^S values for Ca^+ and Sr^+ arise from negative oscillator strengths of the transitions to $(n+1)s_{1/2}$ and nd_j. For $4p_j$ states in Ca^+, cancellations in the sum lead to small α_1^S values, and consistency with RCICP and DFCP is poor. Moreover, the *ab initio* works do not agree with each other. Better agreement is found between α_1^T values of $4p_{3/2}$. For $5p_j$ states in Sr^+, excellent consistency is obtained with RCICP. Results are in good agreement with *ab initio* methods for α_1^S, while the present α_1^T value of $5p_{3/2}$ is around 8% smaller because the matrix element of $5s_{1/2} \rightarrow 5p_{3/2}$ is smaller. Only one *ab initio* calculation is available for $6p_j$ states in Ba^+. The agreement is poor (10% difference) for $6p_{1/2}$. For $6p_{3/2}$, α_1^S values agree well, while α_1^T results disagree because of oscillator strength cancellations associated with a higher uncertainty.

2. Quadrupole polarizabilities

The ground $(n+1)s_{1/2}$ quadrupole polarizabilities involve $n'd_{3/2,5/2}$ states. The present values agree very well (<1% differences) with DFCP [4] for Ca^+ and with RCICP [9] for Sr^+,

TABLE VI. $2E1$ decay rates, W_{2E1} (in s^{-1}), of the $nd_j \rightarrow (n+1)s_{1/2}$ transitions in Ca$^+$ ($n=3$), Sr$^+$ ($n=4$), and Ba$^+$ ($n=5$). DHF-LMM and DHFCP-LMM values are compared with results from Refs. [38] and [76].[a] Uncertainties in the last digits are given within parentheses. Powers of 10 are indicated within brackets.

	W_{2E1} (s^{-1})			
	LMM		Refs. [38,76][a]	
Transition	DHF	DHFCP	DHF	All order
		Ca$^+$		
$3d_{3/2} \rightarrow 4s_{1/2}$	3.446 [−3]	1.030(2) [−4]	3.458 [−3]	9.800 [−5]
$3d_{5/2} \rightarrow 4s_{1/2}$	3.392 [−3]	1.047(2) [−4]	3.404 [−3]	9.945 [−5]
		Sr$^+$		
$4d_{3/2} \rightarrow 5s_{1/2}$	2.765 [−3]	3.465(11) [−4]	2.777 [−3]	3.525 [−4]
$4d_{5/2} \rightarrow 5s_{1/2}$	2.704 [−3]	3.753(11) [−4]	2.718 [−3]	3.807 [−4]
		Ba$^+$		
$5d_{3/2} \rightarrow 6s_{1/2}$	7.359 [−6]	1.446(9) [−7]	7.384 [−6]	1.538 [−7]
$5d_{5/2} \rightarrow 6s_{1/2}$	1.005 [−5]	3.851(25) [−7]	1.013 [−5]	4.039 [−7]

[a] Corrected values [76]; a factor $1/2$ is missing in Ref. [38].

while no reference value is available with these approaches for Ba$^+$. The comparison with *ab initio* methods shows that the present values are a few percents lower, for the same reason as for dipole polarizabilities. The Sr$^+$ experimental value from Ref. [74] is clearly incompatible with the theoretical works, while for Ba$^+$ the experimental result from Ref. [75] is in favor of the *ab initio* number, matching within the experimental uncertainties.

The nd_j quadrupole polarizabilities involve $n's_{1/2}$, $n'd_{3/2,5/2}$,$n'g_{7/2}$ states and additional $n'g_{9/2}$ states for $nd_{5/2}$. Hence, nd_j intermediate states must be excluded from the sum over n' in the nd_j polarizability. The present values for Ca$^+$ differ from the DFCP results by 4% and do not match with RCICP within the theoretical uncertainties for Sr$^+$. The agreement with other semiempirical approaches is thus poor. *Ab initio* values are only available for $nd_{5/2}$ states. The level of agreement ranges from 5% to 9% for Ca$^+$ and below 5% for Sr$^+$. Note that no reference number for the $5d_j$ states in Ba$^+$ is available for comparison.

The $(n+1)p_j$ quadrupole polarizabilities involve $n'p_{3/2}$,$n'f_{5/2}$ states, and additional $n'p_{1/2}$,$n'f_{7/2}$ states for $(n+1)p_{3/2}$. Hence, $(n+1)p_{3/2}$ intermediate states must be excluded from the sum over n' in the $(n+1)p_{3/2}$ polarizability. Excellent consistency (0.2% differences) with DFCP and RCICP is obtained for Ca$^+$, and the values agree very well within the theoretical uncertainties for Sr$^+$. As for the $5d_j$ states, no reference number for the $6p_j$ states in Ba$^+$ is available for comparison.

D. Calculations of decay rates and lifetimes

Table VI displays $2E1$ decay rates, W_{2E1} (in s^{-1}), of the $nd_j \rightarrow (n+1)s_{1/2}$ transitions in Ca$^+$ ($n=3$), Sr$^+$ ($n=4$), and Ba$^+$ ($n=5$) ions. The $nd_{3/2} \rightarrow (n+1)s_{1/2}$ transitions involve $n'p_{1/2,3/2}$ intermediate states, while the $nd_{5/2} \rightarrow (n+1)s_{1/2}$ transitions only involve $n'p_{3/2}$ states. The DHF-LMM and DHFCP-LMM results are computed in the length gauge with $N_c = N_v = N' = 50$ Lagrange functions. The integral over ω_1 is evaluated with $N_{\omega_1} = 50$ mesh points. Significant digits are estimated by increasing N' from 50 to 80 and by comparing results from M I and M II. Better agreement between M I and M II is obtained for DHFCP-LMM results, since DHF-LMM energies differ more significantly between both integration methods. As for Tables IV and V, using the second set of core dipole polarizabilities enables us to estimate theoretical uncertainties on the DHFCP-LMM values displayed in Table VI.

As mentioned in Sec. I, only one prior calculation has been carried out in these ions [38] using the *ab initio* relativistic single-double all-order method. The comparison with the present results enabled detection that a factor $1/2$ was missing in Table I of Ref. [38]. Indeed, both approaches led to comparable differential decay rates $dW_{2E1}/d\omega_1$, and the only source of error was a wrong choice of bounds for the integration over ω_1. A corrigendum has recently been published in Ref. [76].

The DHF-LMM results agree very well with corrected reference values, since both calculations are based on an *ab initio* method. The differences range from 0.4% to 0.5%, apart from 0.8% for the $5d_{5/2} \rightarrow 6s_{1/2}$ transition in Ba$^+$. By contrast, differences between the DHFCP-LMM results and corrected all-order values are one order of magnitude higher, ranging from 1.4% to 6.0% depending on the studied ion. However, the overall agreement is highly satisfying, keeping in mind that semiempirical results are compared to an *ab initio* method that explicitly includes single- and double-electron excitations to all orders of perturbation theory. Besides, the present study leads to the same conclusion as in Ref. [38], i.e., that the DHF values of the $2E1$ decay rates are strongly modified by the inclusion of electron correlation. Indeed, the DHF calculation overestimates the rates by factors of 10–50.

Table VII displays lifetimes, τ (in s), and multipole contributions to the transition rates, W (in s^{-1}), of the nd_j states in Ca$^+$ ($n=3$), Sr$^+$ ($n=4$), and Ba$^+$ ($n=5$) ions. The DHFCP-LMM values of the $2E1$ decay rates are taken from Table VI. The DHFCP-LMM values of the $E2$ decay rates are computed in the length gauge with $N_c = N_v = 50$, and $M1$ decay rates are computed with the same parameters. Significant digits of the $E2$ and $M1$ results are estimated by comparison with $N_v = 60$ considering M I and M II, and the comparison of the results from M I and M II allows the precision of the values displayed in Table VII to be assessed. Again, an estimation of theoretical uncertainties of the values displayed in Table VII is obtained by using the second set of core dipole and quadrupole polarizabilities.

DHFCP-LMM results of the total lifetimes τ are compared with other theory and with observation in order to study the accuracy of the present approach. While the cited theoretical references report only on calculations of $E2$ and $M1$ contributions to the lifetimes of the nd_j states, the present work also includes the $2E1$ contributions.

While the $nd_{3/2}$ states can decay only via $nd_{3/2} \rightarrow (n+1)s_{1/2}$ channels, the $nd_{5/2}$ states decay via $nd_{5/2} \rightarrow (n+1)s_{1/2}$ and $nd_{5/2} \rightarrow nd_{3/2}$ channels. $2E1$ decay rates being proportional to ω^6, their contribution is negligible for $nd_{5/2} \rightarrow nd_{3/2}$ ($<10^{-13}$ s^{-1}) but not for $nd_j \rightarrow (n+1)s_{1/2}$. $E2$ decay rates, proportional to ω^5, are dominant for $nd_j \rightarrow (n+1)s_{1/2}$. They are negligible for $nd_{5/2} \rightarrow nd_{3/2}$ in Ca$^+$ and Sr$^+$, but they

TABLE VII. Lifetimes, τ (in s), and multipole contributions to the transition rates, W (in s^{-1}), of the nd_j states in Ca^+ ($n = 3$), Sr^+ ($n = 4$), and Ba^+ ($n = 5$). DHFCP-LMM results of the total lifetimes τ are compared with other theory and experiment. Uncertainties in the last digits are given within parentheses. Powers of 10 are indicated within brackets for W.

	τ (s)			W (s^{-1})		
State	DHFCP-LMM	Other theory	Experiment	Decay channel	Multipole	DHFCP-LMM
			Ca^+			
$3d_{3/2}$	1.154(7)	1.194(11) [34]	1.111(46) [19]	$3d_{3/2} \rightarrow 4s_{1/2}$	$E2$	8.662(49) [−1]
		1.143(1) [4]	1.17(5) [20]		$M1$	1.947(61) [−11]
		1.185(7) [35]	1.20(1) [21]		$2E1$	1.030(2) [−4]
		1.196(11) [17]	1.176(11) [17]		$\sum W$	8.663(49) [−1]
		1.16 [36]	1.113(45) [22]			
$3d_{5/2}$	1.124(6)	1.163(11) [34]	1.174(10) [24]	$3d_{5/2} \rightarrow 4s_{1/2}$	$E2$	8.892(49) [−1]
		1.114(1) [4]	1.09(5) [20]		$2E1$	1.047(2) [−4]
		1.110(9) [35]	1.168(7) [21]	$3d_{5/2} \rightarrow 3d_{3/2}$	$E2$	2.207(28) [−13]
		1.165(11) [17]	1.168(9) [17]		$M1$	2.422(11) [−6]
		1.14 [36]	1.100(18) [23]		$\sum W$	8.893(49) [−1]
			Sr^+			
$4d_{3/2}$	0.445(3)	0.437(14) [34]	0.435(4) [25]	$4d_{3/2} \rightarrow 5s_{1/2}$	$E2$	2.245(18)
		0.4442(67) [9]	0.435(4) [26]		$M1$	9.223(27) [−11]
		0.441(3) [10]	0.455(29) [26]		$2E1$	3.465(11) [−4]
		0.426(8) [35]	0.395(38) [27]		$\sum W$	2.245(19)
$4d_{5/2}$	0.398(3)	0.3945(22) [34]	0.372(25) [28]	$4d_{5/2} \rightarrow 5s_{1/2}$	$E2$	2.509(20)
		0.3974(59) [9]	0.408(22) [26]		$2E1$	3.753(11) [−4]
		0.394(3) [10]	0.3908(16) [29]	$4d_{5/2} \rightarrow 4d_{3/2}$	$E2$	1.130(19) [−9]
		0.357(12) [35]	0.347(11) [30]		$M1$	2.378(1) [−4]
			0.345(33) [27]		$\sum W$	2.510(20)
			Ba^+			
$5d_{3/2}$	83.86(15)	81.4(14) [34]	79.8(46) [31]	$5d_{3/2} \rightarrow 6s_{1/2}$	$E2$	1.192(3) [−2]
		81.5(12) [11]	89.4(156) [18]		$M1$	2.696(26) [−11]
		82.0 [18]			$2E1$	1.446(9) [−7]
		80.086(714) [35]			$\sum W$	1.192(3) [−2]
		81.5 [37]				
$5d_{5/2}$	31.09(4)	30.34(48) [34]	31.2(9) [32]	$5d_{5/2} \rightarrow 6s_{1/2}$	$E2$	2.662(5) [−2]
		30.3(4) [11]	34.5(35) [28]		$2E1$	3.851(25) [−7]
		31.6 [18]	32.0(46) [18]	$5d_{5/2} \rightarrow 5d_{3/2}$	$E2$	2.622(10) [−7]
		29.856(296) [35]	32(5) [33]		$M1$	5.543(2) [−3]
		30.3 [37]			$\sum W$	3.216(5) [−2]

become comparable to $2E1$ contributions for $5d_{5/2} \rightarrow 5d_{3/2}$ in Ba^+. $M1$ decay rates, proportional to ω^3, are negligible for $nd_{3/2} \rightarrow (n+1)s_{1/2}$ but not for $nd_{5/2} \rightarrow nd_{3/2}$. However, their contribution is only significant to the $5d_{3/2}$ lifetime in Ba^+.

Taking the inverse of the total decay rates W (in s^{-1}) yields the total lifetimes τ (in s). The DHFCP-LMM results agree very well ($<1\%$ differences) with DFCP [4] for Ca^+ and RCICP [9] for Sr^+, and good consistency is found with various *ab initio* calculations for these two ions. Among them, 0.5%–5% differences are obtained with the very recent work using the relativistic all-order method [34]. For each nd_j lifetime of Ca^+ and Sr^+, the present results lie within the uncertainties of at least one experiment, and the discrepancies with the other experimental values are not high. It should be noticed that discrepancies also occur among theoretical and experimental values as well as between the two of them. Lifetimes are longer in Ba^+ than in Ca^+ and Sr^+. Comparison of the present calculation of $5d_j$ lifetimes with Ref. [34] yields 0.9%–5% differences, in the same range as in Ca^+ and Sr^+. Values vary from one to two units between *ab initio* calculations, and the large experimental uncertainties due to the long lifetimes do not allow discrimination between the different works.

V. CONCLUSIONS

This work presents DHFCP-LMM calculations of polarizabilities, one- and two-photon decay rates, and associated lifetimes in Ca^+, Sr^+, and Ba^+ ions. Two integration methods are devised to compute two-electron Slater integrals, and the comparison of their results allows the precision of the values displayed in the tables to be assessed. In addition, the effect of variations in the values of the core dipole and quadrupole polarizabilities on the final results is studied, which enables estimation of theoretical uncertainties on the latter.

The core orbitals are defined by a closed-shell DHF calculation with the GRASP2K package and are projected on Lagrange bases. The single valence electron is described in the frozen-core approximation by a Dirac-like Hamiltonian involving a CP potential to simulate the core-valence electron correlation. Comparing with GRASP2K results, the accuracy on core energies is $\sim 10^{-7}$, while the one on DHF valence energies is $\sim 10^{-5}$ for the five lowest states of each ion. With the inclusion of V_{CP}, calculated energies are fitted with relative errors $< 10^{-7}$ in comparison with observation.

Turning to dipole and quadrupole polarizabilities, the agreement with other semiempirical approaches is excellent for Ca^+ and Sr^+, while no such reference value exists for Ba^+. Overall good agreement is obtained with *ab initio* methods and observation, although semiempirical approaches underestimate the ground-state polarizabilities by a few percents. The principal limitation of the accuracy on polarizabilities with such approaches lies in the accuracy of the core polarizabilities, which have to be computed with an independent method.

For the $2E1$ $nd_j \rightarrow (n+1)s_{1/2}$ decay rates, a comparison with Refs. [38] and [76] shows that both DHF results agree very well with each other and that a satisfying agreement is obtained between the DHFCP-LMM and all-order values. Both works conclude that the DHF values are strongly modified by the inclusion of electron correlation.

The lifetimes estimation of the metastable nd_j states involves the study of the competition between the $E2$, $M1$, and $2E1$ decay channels. The present results agree very well with other semiempirical approaches for Ca^+ and Sr^+, and overall good consistency is found with *ab initio* calculations and experiments. Results vary more significantly between calculations for Ba^+, and the few existing experiments are associated with large uncertainties. Moreover, the contribution of the $2E1$ processes to the total decay rates of nd_j states is negligible (0.001%–0.01%) at the present level of theoretical and experimental accuracy. This conclusion had already been reached in Ref. [38]. Estimating more accurate lifetimes for the nd_j metastable states in these three ions currently represents a difficult task. Other decay processes are expected to compete with the $E2$, $M1$, and $2E1$ channels, such as magnetic-field-induced transitions (MIT), and hyperfine-induced transitions (HIT) for odd-A isotopes of these three ions. These processes are likely to modify the existing theoretical lifetime values. Besides, high-precision experimental results are urgently needed to test the theoretical predictions of the $5d_j$ lifetimes in Ba^+.

Our work is based on a fully relativistic version of the semiempirical-core-potential approach. As such, it is an approximate method, where the comparison with experiments and other theories should in principle provide an assessment of the errors due to physical effects that are not included in the model. As illustrated by Tables IV–VII, estimating more realistic theoretical uncertainties based on such comparisons would be statistically meaningless, due to the dispersion of *ab initio* and experimental values.

Comparison with other theory and observation shows that the DHFCP-LMM method provides a simple and efficient way for evaluating properties of alkalilike ions involving an infinite number of intermediates states, such as relativistic polarizabilities and two-photon decay rates. By using the LMM, which allows a simple computation of one-body matrix elements, and by developing Gauss-quadrature-based methods to accurately evaluate the two-electron Slater integrals, precise results are obtained with small computing times and memory requirements. Besides, the use of the GRASP2K package for core-orbital calculations reduces the code-development effort to only single-valence-electron calculations. The present approach can play a role in further improvement of theoretical nd_j lifetimes in these three ions. It can also be used to study a variety of heavy alkalilike systems, such as Cs, Fr, Ra^+, and Yb^+, for which theoretical results and experimental data are available for comparison, or others for which information is not available. Dynamic polarizabilities, hyperpolarizabilities, and dispersion coefficients involved in long-range interactions between pairs of atoms can be studied in various alkalilike systems. From a methodological point of view, the LMM could also offer some computational advantages for estimating other properties involving an infinite number of intermediate states, such as atomic electric dipole moments and parity nonconservation amplitudes.

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APPENDIX: TWO-ELECTRON SLATER INTEGRALS ON LAGRANGE MESHES

Starting with M I, let us introduce in Eq. (33) the expansion $Y_q^k(jc;r) = \bar{h}^{-1/2}\sum_{l=1}^{\bar{N}} y_l\ \hat{f}_l^{(\bar{\alpha}=0)}(r/\bar{h})$, satisfying the boundary condition $Y_q^k(jc;0) = 0$ since $\hat{f}_l^{(0)}(0) = 0$. Projecting the left-hand side of Eq. (33) on $\bar{h}^{-1/2}\hat{f}_{l'}^{(0)}(r/\bar{h})$ leads to [45]

$$\bar{h}^{-2}\left\{\sum_{l\neq l'}^{\bar{N}} y_l\left[(-1)^{l-l'+1}\frac{\bar{x}_l+\bar{x}_{l'}}{\sqrt{\bar{x}_l\bar{x}_{l'}}(\bar{x}_l-\bar{x}_{l'})^2}\right] + y_{l'}\left[\frac{\bar{x}_{l'}^2-2(2\bar{N}+1)\bar{x}_{l'}-4}{12\bar{x}_{l'}^2}-\frac{k(k+1)}{\bar{x}_{l'}^2}\right]\right\} \qquad \text{(A1)}$$

for $l' = 1$ to $\bar{N}$, using a Gauss quadrature with parameters $\bar{N} = N_v + N_c$, $\bar{h} = 2h_c$, and $\bar{\alpha} = 0$. The first two values are deduced from expression (32), while the Schrödinger-like form of Eq. (33) requires an integer value of $\bar{\alpha}$ to reproduce the exact behavior of $Y_q^k(jc;r)$ near the origin. Projecting the right-hand side of Eq. (33) on $\bar{h}^{-1/2}\hat{f}_{l'}^{(0)}(r/\bar{h})$ leads to

$$-(\bar{h}h_v)^{-1/2}\sum_{m=1}^{N_G}\tilde{\lambda}_m\ \hat{f}_{l'}^{(0)}(\tilde{h}\tilde{x}_m/\bar{h})\frac{2k+1}{\tilde{x}_m} \times Q_c(\tilde{h}\tilde{x}_m)\hat{f}_j^{(\alpha_v)}(\tilde{h}\tilde{x}_m/h_v) \qquad \text{(A2)}$$

for $l' = 1$ to $\bar{N}$, using a Gauss quadrature with parameters $N_G > N_v + N_c$, $\tilde{h} = 4h_vh_c/(3h_v + 2h_c)$, and $\tilde{\alpha} = (\alpha_v + \alpha_c)/2$. The equality of Eqs. (A1) and (A2) defines an $\bar{N}\times\bar{N}$ algebraic system which is solved with a standard technique.

For the case $k = 0$, the expansion of $Y_q^0(jc;r)$ is not able to reproduce the asymptotic behavior $Y_q^0(jc;\infty) \neq 0$ since $\hat{f}_l^{(0)}(r/\bar{h}) \rightarrow 0$ as $r \rightarrow \infty$. To overcome this issue, the function $Y_q^0(jc;\infty)\,(1 - e^{-r})$ is subtracted from $Y_q^0(jc;r)$ in Eq. (33), and Eq. (A2) is modified to include the Gauss quadrature of $Y_q^0(jc;\infty) \int_0^\infty \bar{h}^{-1/2} \hat{f}_{l'}^{(0)}(r/\bar{h})\, e^{-r}\, dr$. $Y_q^0(jc;r)$ is recovered by adding back $Y_q^0(jc;\infty)\,(1 - e^{-r})$ to the solution of the modified algebraic system. Once $Y_q^k(jc;r)$ is known, integral (34) is expressed using a Gauss quadrature with the same parameters as in (A2):

$$R_{\mathrm{pq}}^k(ic,cj) \approx h_v^{-1/2} \sum_{m=1}^{N_G} \tilde{\lambda}_m\, \hat{f}_i^{(\alpha_v)}(\tilde{h}\tilde{x}_m/h_v) P_c(\tilde{h}\tilde{x}_m) \times \frac{1}{\tilde{x}_m}\, Y_q^k(jc;\tilde{h}\tilde{x}_m). \tag{A3}$$

Turning to M II, let us start with the integral over r in Eq. (37). Defining $\bar{h} \equiv 2h_v h_c/(h_v + h_c)$, the integrand reads

$$(r + r_2)^{(\alpha_v+\alpha_c)/2-k}\, \mathcal{P}_{N_v+N_c-1}(r + r_2)\, e^{-(r+r_2)/\bar{h}}, \tag{A4}$$

where $\mathcal{P}_{N_v+N_c-1}$ is a polynomial of degree $N_v + N_c - 1$ and the first factor is nonpolynomial. Expression (A4) suggests that computing the integral over r by the Gauss-Laguerre quadrature with weight function $\exp(-r/\bar{h})$ and $N_G > (N_v + N_c)/2$ points should be efficient. Denoting the associated abscissae and weights by $\bar{h}\bar{x}_m$ and $\bar{h}\bar{\lambda}_m$ (with $m = 1$ to N_G) yields

$$\int_0^\infty \frac{\hat{f}_i^{(\alpha_v)}[(r + r_2)/h_v] P_c(r + r_2)}{(r + r_2)^{k+1}}\, dr \approx \bar{h} \sum_{m=1}^{N_G} \bar{\lambda}_m \frac{\hat{f}_i^{(\alpha_v)}[(\bar{h}\bar{x}_m + r_2)/h_v] P_c(\bar{h}\bar{x}_m + r_2)}{(\bar{h}\bar{x}_m + r_2)^{k+1}}. \tag{A5}$$

For each term of the sum over m, the integrand of the integral over r_2 can be written as

$$(\bar{h}\bar{x}_m + r_2)^{(\alpha_v+\alpha_c)/2-k}\, r_2^{(\alpha_v+\alpha_c)/2}\, \tilde{\mathcal{P}}_{2N_v+2N_c+k-1}(r_2)\, e^{-r_2/\tilde{h}}, \tag{A6}$$

where $\tilde{\mathcal{P}}_{2N_v+2N_c+k-1}$ is a polynomial of degree $2N_v + 2N_c + k - 1$ and $\tilde{h} \equiv \bar{h}/2$. This expression incites us to evaluate the integral over r_2 by a Gauss-Laguerre quadrature with weight function $r_2^{(\alpha_v+\alpha_c)/2} \exp(-r/\tilde{h})$ and $N'_G > N_v + N_c + k/2$ points. Let us denote by $\tilde{h}\tilde{x}_{m'}$ and $\tilde{h}\tilde{\lambda}_{m'}$ (with $m' = 1$ to N'_G) the abscissae and weights of this Gauss quadrature. The integral $\mathcal{R}_{\mathrm{pq}}^k(ic,cj)$ given by Eq. (37) reads, finally,

$$\begin{aligned} \mathcal{R}_{\mathrm{pq}}^k(ic,cj) &\approx h_v^{-1}\bar{h}\tilde{h} \sum_{m'=1}^{N'_G} \tilde{\lambda}_{m'}\, \hat{f}_j^{(\alpha_v)}(\tilde{h}\tilde{x}_{m'}/h_v) Q_c(\tilde{h}\tilde{x}_{m'})\, (\tilde{h}\tilde{x}_{m'})^k \\ &\quad \times \sum_{m=1}^{N_G} \bar{\lambda}_m \frac{\hat{f}_i^{(\alpha_v)}[(\bar{h}\bar{x}_m + \tilde{h}\tilde{x}_{m'})/h_v] P_c(\bar{h}\bar{x}_m + \tilde{h}\tilde{x}_{m'})}{(\bar{h}\bar{x}_m + \tilde{h}\tilde{x}_{m'})^{k+1}}. \end{aligned} \tag{A7}$$

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