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# Properties of metastable alkaline-earth-metal atoms calculated using an accurate effective core potential

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The first three electronically excited states in the alkaline-earth-metal atoms magnesium, calcium, and strontium comprise the $(nsnp)^3P_J^o(J=0,1,2)$ fine-structure manifold. All three states are metastable and are of interest for optical atomic clocks as well as for cold-collision physics. An efficient technique—based on a physically motivated potential that models the presence of the ionic core—is employed to solve the Schrödinger equation for the two-electron valence shell. In this way, radiative lifetimes, laser-induced clock shifts, and long-range interaction parameters are calculated for metastable Mg, Ca, and Sr.

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## I. INTRODUCTION

Effectively, alkaline-earth-metal atoms are two-electron atoms, at least at low excitation energies. Alkaline-earth-metal atoms display—like true two-electron systems—spin singlet and triplet level manifolds, which give rise to narrow intercombination transitions. However, since all alkaline-earth-metal atoms possess a closed *K* shell, their level structure does also show notable differences to that of heliumlike systems.

In this work we focus on the lowest $^3P^o$ manifold, with fine-structure components $J=0,1,2$, in the alkaline-earth-metal atoms magnesium, calcium, and strontium. These three fine-structure states represent the first three electronically excited states in these species. The excitation energies, relative to the $^1S_0$ ground state, are reproduced in Table I [1]. The table illustrates that for all three atoms, the excitation energies correspond to optical wavelengths accessible by modern laser sources. However, that does not imply the fine-structure components of the $^3P^o$ manifold are easy to excite. The transition from the ground state to the $^3P_1^o$ is spin forbidden, that to the $^3P_0^o$ and the $^3P_2^o$ states is, additionally, in general electric-dipole-forbidden. (See Ref. [2] for a thorough introduction to the topic of forbidden transitions in one- and two-electron atoms.) This makes the $^3P^o$ manifold in the alkaline-earth-metal atoms interesting for several applications in the physics of cold atoms.

The unique level structure triggered advances in laser-cooling technology and allowed to explore processes in a magneto-optical trap at a new level [3–10]. Current successful approaches to an optical frequency standard using neutral, laser-cooled atoms are based on the relatively small linewidth of the $^1S_0\rightarrow{}^3P_1^o$ transition in calcium [11–13]. Significant improvement in accuracy is expected from the strategy of storing fermionic $^{87}$Sr atoms in an optical lattice and probing the $^1S_0\rightarrow{}^3P_0^o$ transition [14–18].

TABLE I. The excitation energies, in eV, of the first three excited states in the alkaline-earth-metal atoms magnesium $(3s3p)$, calcium $(4s4p)$, and strontium $(5s5p)$. The data are taken from Ref. [1].

| | Mg | Ca | Sr |
|---|---|---|---|
| $^3P_0^o$ | 2.71 | 1.88 | 1.78 |
| $^3P_1^o$ | 2.71 | 1.89 | 1.80 |
| $^3P_2^o$ | 2.72 | 1.90 | 1.85 |

Due to the prevalence of stable alkaline-earth-metal isotopes with vanishing nuclear angular momentum, it is possible to investigate cold collisions and to perform photoassociation spectroscopy free of any complications from hyperfine structure [19–23]. However, it is not possible to form a quantum-degenerate gas [24–26] of ground-state alkaline-earth-metal atoms by employing evaporative cooling in a pure magnetic trap. Therefore, it has been suggested to make use of the long-lived $^3P_2^o$ state [27,28]. Several groups have already succeeded in magnetically trapping $^3P_2^o$ alkaline-earth-metal atoms [29–32]. Theoretical studies have uncovered that anisotropic interactions between $^3P_2^o$ atoms in an external magnetic field lead to unexpectedly rich collision physics [33–35].

It is the purpose of this paper to provide a concise overview of the properties of Mg, Ca, and Sr in the $^3P_0^o$, $^3P_1^o$, and $^3P_2^o$ states. In Sec. II we describe our specific approach to the electronic-structure problem of effective two-electron atoms. The method adopted is not only numerically efficient, it can supply atomic data at a level of accuracy comparable with high-level *ab initio* calculations. Section III is devoted to a discussion of spontaneous decay of the individual fine-structure components of the $^3P^o$ manifold. Then, in Sec. IV, we calculate the effect of the dynamic Stark shift on the $^1S_0\rightarrow{}^3P_0^o$ clock transition. Parameters characterizing the long-range interaction between metastable alkaline-earth-metal atoms are the subject of Sec. V. We conclude with Sec. VI. Unless indicated otherwise, atomic units are used throughout.

## II. TREATMENT OF THE ELECTRONIC-STRUCTURE PROBLEM

Our strategy toward solving the electronic-structure problem of alkaline-earth-metal atoms involves the following steps [36–38]. We first treat the effective one-electron eigenvalue problem of the singly charged alkaline-earth-metal ion with a single valence electron. This valence electron moves in a one-particle model potential that reproduces the valence excitation energies of the monocation. We represent the radial degree of freedom of the electronic wave function in a finite-element basis set. From the solutions of the one-electron problem, two-electron basis functions are constructed. The effective two-electron Hamiltonian, which describes the neutral atom and which fully incorporates valence-electron correlation, is represented in this basis and diagonalized. In this way, eigenenergies and eigenvectors of the two-electron valence shell are obtained.

### A. One-particle Hamiltonian

When treating the effective one-electron problem of the monocation, we employ the one-electron Hamiltonian

$$h_1 = -\frac{1}{2}\nabla^2 + V + V^{(\mathrm{so})}. \tag{1}$$

The operator $V$ represents the electrostatic field generated by the noble-gas-like core. This is a central field. However, an explicit dependence of the associated potential on the orbital angular momentum quantum number $l$ must be included to take account of the fact that electrons with $l=0$ dive deep into the core and experience relativistic effects (orbital contraction). Such scalar relativistic effects decrease with the average distance from the nucleus and thus with $l$. Therefore, we assume that the spin-angular representation of $V$ can be written as

$$\langle j,m_j,l,s|V|j',m_{j'},l',s\rangle = \delta_{j,j'}\delta_{m_j,m_{j'}}\delta_{l,l'}V_l(r). \tag{2}$$

The quantum numbers $j$ and $m_j$ refer to the total angular momentum of the valence electron, $s=1/2$ denotes its spin. In this work, the following parametrization of $V_l(r)$ is used:

$$V_l(r) = -\frac{1}{r}\{2 + (Z-2)\exp(-\alpha_{l,1}r) + \alpha_{l,2}r\,\exp(-\alpha_{l,3}r)\} - \frac{\alpha_{\mathrm{cp}}}{2r^4}\{1-\exp[-(r/r_l)^6]\}. \tag{3}$$

$Z$ is the nuclear charge. The parameters $\alpha_{l,1}$, $\alpha_{l,2}$, $\alpha_{l,3}$, $\alpha_{\mathrm{cp}}$, and $r_l$ are listed in Ref. [38]. The potential $V_l(r)$ describes the interaction of the valence electron with the ionic core at various length scales. For very large distances from the core, the electron is attracted by a point charge of charge +2. As the electron comes closer, the ionic core responds to the presence of the electron and becomes polarized, as expressed by the term proportional to $\alpha_{\mathrm{cp}}/r^4$. Below $r=r_l$, the electron dives into the core. The parameters $\alpha_{l,1}$, $\alpha_{l,2}$, and $\alpha_{l,3}$ mediate the transition from the exterior region of the core to the interior, where at very small length scales the electron interacts with the unscreened charge $Z$.

Spin-orbit interaction is represented in Eq. (1) by the operator $V^{(\mathrm{so})}$,

$$\langle j,m_j,l,s|V^{(\mathrm{so})}|j',m_{j'},l',s\rangle = \delta_{j,j'}\delta_{m_j,m_{j'}}\delta_{l,l'}V_{l,j}^{(\mathrm{so})}(r), \tag{4}$$

where

$$V_{l,j}^{(\mathrm{so})}(r) = \{j(j+1) - l(l+1) - s(s+1)\} \times \frac{\alpha^2}{4r}\frac{dV_l}{dr}\left[1-\frac{\alpha^2}{2}V_l\right]^{-2}, \tag{5}$$

and $\alpha \approx 1/137.036$ is the fine-structure constant.

The eigenstates of $h_1$ can now be written as

$$\psi = \frac{u_{l,j}(r)}{r}|j,m_j,l,s\rangle, \tag{6}$$

and we can focus on solving the radial equation

$$\overline{h_{l,j}}u_{l,j}(r) = \varepsilon_{l,j}u_{l,j}(r), \quad u_{l,j}(0)=0, \tag{7}$$

$$\overline{h_{l,j}} = -\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_l(r) + V_{l,j}^{(\mathrm{so})}(r). \tag{8}$$

To this end, we apply a technique based on finite elements [39–44].

### B. Finite-element basis

For the radial degree of freedom, we introduce a quadratically spaced grid of $N+1$ grid points between $r=0$ and $r=r_{\mathrm{max}}$, i.e., $r_i=r_{\mathrm{max}}i^2/N^2$, $i=0,\ldots,N$. In each interval $[r_i,r_{i+1}]$, six unique, linearly independent fifth-order Hermite interpolating polynomials can be constructed that satisfy the boundary conditions

$$\left.\frac{d^kP_{j,i}(r)}{dr^k}\right|_{r=r_i} = \delta_{j,k},$$

$$\left.\frac{d^kP_{j,i}(r)}{dr^k}\right|_{r=r_{i+1}} = 0,$$

$$\left.\frac{d^kQ_{j,i}(r)}{dr^k}\right|_{r=r_{i+1}} = \delta_{j,k},$$

$$\left.\frac{d^kQ_{j,i}(r)}{dr^k}\right|_{r=r_i} = 0, \tag{9}$$

where $j,k=0,1,2$. The functions are defined to vanish everywhere outside $[r_i,r_{i+1}]$. Using the definitions

$$g_0(r) = f(r)^3[6f(r)^2 - 15f(r) + 10],$$

$$g_1(r) = \Delta r f(r)^3[3f(r)^2 - 7f(r) + 4],$$

$$g_2(r) = \tfrac{1}{2}\Delta r^2 f(r)^3[f(r)-1]^2, \tag{10}$$

we have, for $r\in[r_i,r_{i+1}]$ and $j=0,1,2$,

$$P_{j,i}(r) = g_j(r), \quad \Delta r = r_{i+1} - r_i, \quad f(r) = -\frac{r-r_{i+1}}{\Delta r} \tag{11}$$

and

$$Q_{j,i}(r) = g_j(r), \quad \Delta r = r_i - r_{i+1}, \quad f(r) = -\frac{r - r_i}{\Delta r}. \tag{12}$$

These formulas correct some misprints in Eq. (49) of Rescigno *et al.*[43]. Three continuous basis functions, with continuous first and second derivatives, can now be associated with grid point $r_i$ $(i=1,\dots,N-1)$:

$$B_{j,i}(r) = P_{j,i}(r) + Q_{j,i-1}(r), \quad j = 0,1,2. \tag{13}$$

Using these, the function value at grid point $r_i$, the first derivative, and the second derivative of any wave function can be represented. At the end points, $r_0$ and $r_N$, we set

$$B_{0,0}(r) = 0, \quad B_{j,0}(r) = P_{j,0}(r), \quad j = 1,2, \tag{14}$$

which is consistent with the boundary condition specified in Eq. (7), and

$$B_{0,N}(r) = 0, \quad B_{j,N}(r) = Q_{j,N-1}(r), \quad j = 1,2, \tag{15}$$

which selects solutions to Eq. (7) that vanish at $r = r_{\max}$.

The solutions to the eigenvalue problem of $\bar{h}$,

$$\bar{h} u_k(r) = \varepsilon_k u_k(r) \tag{16}$$

(the explicit dependence on angular momentum quantum numbers is suppressed), are found by expanding the eigenfunctions in terms of the finite-element basis functions $B_{j,i}(r)$:

$$u_k(r) = \sum_{i=0}^{N} \sum_{j=0}^{2} \beta_{(j,i),k} B_{j,i}(r). \tag{17}$$

Hence, we have to solve the generalized eigenvalue problem

$$\bar{\boldsymbol{h}}\boldsymbol{\beta}_k = \varepsilon_k \boldsymbol{o}\boldsymbol{\beta}_k, \tag{18}$$

where

$$(\bar{\boldsymbol{h}})_{(j,i),(j',i')} = \int_0^{r_{\max}} dr B_{j,i}(r)\bar{h}B_{j',i'}(r), \tag{19}$$

$$(\boldsymbol{o})_{(j,i),(j',i')} = \int_0^{r_{\max}} dr B_{j,i}(r)B_{j',i'}(r), \tag{20}$$

and

$$(\boldsymbol{\beta}_k)_{(j,i)} = \beta_{(j,i),k}. \tag{21}$$

Since the basis function $B_{j,i}(r)$ vanishes outside $[r_{i-1}, r_{i+1}]$, both matrices, $\bar{\boldsymbol{h}}$ and $\boldsymbol{o}$, have a simple banded structure with small bandwidth. The high degree of sparsity is ideal for iterative solvers [45]. Using the Lanczos-based package ARPACK [46], we calculate—for each valid combination of angular momentum quantum numbers $l$ and $j$—the first 18 eigenfunctions outside the core shells. In other words, solutions associated with inner shells are skipped. Thus, the selected valence-electron solutions display correct nodal behavior.

### C. Two-particle Hamiltonian

We describe the neutral atom employing the effective two-electron Hamiltonian

$$h_2 = h_1(1) + h_1(2) + \frac{1}{|\boldsymbol{x}_1 - \boldsymbol{x}_2|}, \tag{22}$$

i.e., within the approach we take, both valence electrons move in the field of the model potential $V$ [Eqs. (2) and (3)], are subject to spin-orbit coupling through $V^{(\mathrm{so})}$ [Eqs. (4) and (5)], and experience mutual Coulomb repulsion.

In order to tackle the eigenvalue problem of $h_2$, we construct two-electron basis functions, in $jj$ coupling, from the solutions of the one-electron problem:

$$\Phi = \mathcal{A}\frac{u_{l_1,j_1}(r_1)}{r_1}\frac{u_{l_2,j_2}(r_2)}{r_2}\sum_{m_{j_1},m_{j_2}} C(j_1 j_2 J; m_{j_1} m_{j_2} M)|j_1, m_{j_1}, l_1, s_1\rangle \times |j_2, m_{j_2}, l_2, s_2\rangle, \tag{23}$$

where $\mathcal{A}$ is an antisymmetrization operator and $C(j_1 j_2 J; m_{j_1} m_{j_2} M)$ is a Clebsch-Gordan coefficient. The total electronic angular momentum, $J$, the associated projection $M$ as well as the atomic parity $\Pi = (-1)^{l_1+l_2}$, are the only good quantum numbers in the two-electron problem, Eq. (22). The matrix representation of $h_1(1)+h_1(2)$—the Hamiltonian of two noninteracting valence electrons—in the basis of the two-electron functions is, of course, diagonal. Using the familiar relation [47]

$$\frac{1}{|\boldsymbol{x}_1 - \boldsymbol{x}_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}(\vartheta_1, \varphi_1) Y_{lm}^*(\vartheta_2, \varphi_2),$$

$$r_< = \min\{r_1, r_2\}, r_> = \max\{r_1, r_2\}, \tag{24}$$

together with standard Wigner-Racah algebra [48–50], the matrix of the electron-electron interaction term in Eq. (22) can be calculated.

The resulting matrix representation of $h_2$ is sufficiently small to allow for full numerical diagonalization. Properties of the valence shell can now be computed from the spectrum and eigenvectors of this matrix. In order to estimate the accuracy of our calculations, we first calculate the physical quantity of interest (a radiative decay rate, for example), ensuring convergence with respect to all basis set parameters. In this step, the eigenenergies and the relevant matrix elements with respect to the eigenvectors are taken from our calculations. Then we recalculate that physical quantity by replacing the *energies* of the most important states by experimental energies taken from Ref. [1]. Finally, we quote the result based on the experimental energies together with an error estimate given by the difference from the result calculated using theoretical energies.

## III. RADIATIVE DECAY RATES

### A. ${}^3P_0^o$

The bosonic atoms ${}^{24}$Mg, ${}^{40}$Ca, and ${}^{88}$Sr are by far the most abundant isotopes of magnesium, calcium, and strontium, respectively. The nuclei in these isotopes have vanishing nuclear spin, implying that the quantum number $J=0$ in the $^3P_0^o$ state is exact. As all one-photon operators have a rank greater than zero, the most important way the $^3P_0^o$ state can decay is via an $E1M1$ two-photon process, which, in contrast to $E1E1$, can mediate the parity change between $^3P_0^o$ and $^1S_0$. The $E1M1$ process has been analyzed in detail for the radiative decay of the $^3P_0^o$ state in heavy heliumlike ions [51–53], where this process competes with the usual $E1$ decay. (In heliumlike systems, the $^3P_0^o$ state is not the first excited state.)

The $E1M1$-decay rate from the $^3P_0^o$ state, symbolized by the state vector $|i\rangle$ with energy $E_i$, to the $^1S_0$ ground state $(|f\rangle, E_f)$ can be readily derived within the framework of quantum electrodynamics [54] and is given by

$$\Gamma_{E1M1} = \frac{8}{27\pi}\alpha^6 \int_0^\infty d\omega_1 \omega_1^3 \int_0^\infty d\omega_2 \omega_2^3 \times \left| \sum_{n_+} \frac{\langle f\|M_1\|n_+\rangle\langle n_+\|D\|i\rangle}{E_{n_+}+\omega_1-E_i} + \sum_{n_-} \frac{\langle f\|D\|n_-\rangle\langle n_-\|M_1\|i\rangle}{E_{n_-}+\omega_2-E_i} \right|^2 \delta(E_f+\omega_1+\omega_2-E_i). \tag{25}$$

We use the notation $\langle\cdot\|\cdot\|\cdot\rangle$ to denote a *reduced* matrix element [48–50]. Equation (25) illustrates that the two emitted photons with energies $\omega_1$ and $\omega_2$, respectively, share the available energy, $E_i-E_f$. The decay can proceed in two indistinguishable ways. In one of the two, the $E1$ photon is emitted first, mediated by the electric-dipole operator

$$D_q = -\sum_i r_i C_{1,q}(\vartheta_i,\varphi_i), \tag{26}$$

and a virtual transition to the manifold of states $|n_+\rangle$ with even parity and $J=1$ takes place. (We use the definition $C_{l,q}=\sqrt{4\pi/2l+1}Y_{l,q}$.) The intermediate states are then coupled to the ground state by the magnetic-dipole operator

$$M_{1,q} = -\mu_B(J_q+S_q), \tag{27}$$

$\mu_B$ denoting the Bohr magneton. Alternatively, we first have a virtual $M1$ transition to states $|n_-\rangle$ with odd parity and $J=1$, followed by $E1$ emission. In the case of the lowest $^3P_0^o$ state in Mg, Ca, and Sr, the energy denominators in Eq. (25) differ from zero for all $\omega_1$ and $\omega_2$, so that there are no numerical complications arising from poles.

Our calculated $E1M1$ rates are presented in Table II. They are, not surprisingly, very small throughout. Even in strontium, which decays faster by more than an order of magnitude than calcium and magnesium, the lifetime is about 5800 years. This lifetime is comparable to the half-life of the radioactive isotope $^{14}$C.

The nuclear angular momentum, $I$, in the fermionic isotopes of magnesium, calcium, and strontium differs from zero [55]: $I(^{25}\mathrm{Mg})=5/2$, $I(^{43}\mathrm{Ca})=7/2$, $I(^{87}\mathrm{Sr})=9/2$. The finite nuclear magnetic-dipole moment couples the $^3P_0^o$ state to states of the same parity but with $J=1$. The most important among these states are the energetically lowest $^3P_1^o$ and $^1P_1^o$ states. These can decay directly to the ground state by emission of an $E1$ photon.

TABLE II. Spontaneous decay rate, in s$^{-1}$, of the $^3P_0^o$ state in the alkaline-earth-metal atoms magnesium ($3s3p$), calcium ($4s4p$), and strontium ($5s5p$). The spinless bosonic isotopes can decay only via $E1M1$ two-photon emission. The stable fermionic isotopes—$^{25}$Mg, $^{43}$Ca, and $^{87}$Sr—decay by a hyperfine-induced $E1$ one-photon process.

| | Mg | Ca | Sr |
|---|---|---|---|
| | | Bosonic isotopes | |
| This work | $1.6(1)\times10^{-13}$ | $3.9(2)\times10^{-13}$ | $5.5(3)\times10^{-12}$ |
| | | Fermionic isotopes | |
| This work | $9(3)\times10^{-4}$ | $3(1)\times10^{-3}$ | $9(3)\times10^{-3}$ |
| Ref. [59] | $4.2\times10^{-4}$ | | |
| Ref. [60] | | | $5.5\times10^{-3}$ |
| Ref. [61] | $4.44\times10^{-4}$ | $2.22\times10^{-3}$ | $7.58\times10^{-3}$ |

The interaction of the valence electrons with the magnetic-dipole moment, $\boldsymbol{M}_1^{\mathrm{nuc}}$, and the electric-quadrupole moment, $\boldsymbol{Q}_2^{\mathrm{nuc}}$, of the atomic nucleus is given by the hyperfine-coupling operator [56],

$$V_{\mathrm{hf}} = -\sqrt{3}\alpha\sum_i \left\{ \frac{8\pi}{3}\delta(\boldsymbol{x}_i)[\boldsymbol{s}_i\otimes\boldsymbol{M}_1^{\mathrm{nuc}}]_{0,0} + \frac{1}{r_i^3}[\boldsymbol{l}_i\otimes\boldsymbol{M}_1^{\mathrm{nuc}}]_{0,0} - \frac{\sqrt{10}}{r_i^3}\{[\boldsymbol{C}_2(\vartheta_i,\varphi_i)\otimes\boldsymbol{s}_i]_1\otimes\boldsymbol{M}_1^{\mathrm{nuc}}\}_{0,0} \right\} - \sum_i \frac{\sqrt{5}}{r_i^3}[\boldsymbol{C}_2(\vartheta_i,\varphi_i)\otimes\boldsymbol{Q}_2^{\mathrm{nuc}}]_{0,0}. \tag{28}$$

We employ the notation

$$[\boldsymbol{A}_{k_1}\otimes\boldsymbol{B}_{k_2}]_{K,M} = \sum_{m_1,m_2} C(k_1k_2K;m_1m_2M)A_{k_1,m_1}B_{k_2,m_2} \tag{29}$$

for the rank-$K$ tensor product of tensors $\boldsymbol{A}_{k_1}$ (rank $k_1$) and $\boldsymbol{B}_{k_2}$ (rank $k_2$).

It is not *a priori* clear that the valence-electron wave functions derived from the model potential, Eq. (3), have the correct behavior near the nucleus, even if valence excitation spectra can be well reproduced. In order to check this, we employed the hyperfine-coupling operator $V_{\mathrm{hf}}$ to quantitatively calculate hyperfine parameters for the $(5s5p)$ $^3P_1^o$ and $^3P_2^o$ states in $^{87}$Sr [55]. For $^3P_1^o$ we find $A=-278$ MHz and $B=-30.8$ MHz. This result is in reasonable agreement with an experiment by zu Putlitz [57], who measured $A=-260$ MHz and $B=-35.7$ MHz. Heider and Brink [58] determined the hyperfine parameters for the $^3P_2^o$ state: $A=-213$ MHz and $B=67.2$ MHz. Our calculation gives $A=-231$ MHz and $B=56.5$ MHz. Even though the agreement is not perfect, it indicates that we should be able to calculate the hyperfine-induced coupling of the $^3P_0^o$ state to other electronic levels with an accuracy of about 10%.

Since the hyperfine-coupling operator $V_{\mathrm{hf}}$ [Eq. (28)] is a tensor of rank 0 with respect to rotations of nucleus and electrons, it conserves the total angular momentum of the atom, $F$. Furthermore, for the transition from ${}^3P_0^o$ to ${}^1S_0$, $F=I$. First-order perturbation theory leads to the following formula for the hyperfine-induced spontaneous decay rate:

$$\Gamma_{\mathrm{hf}} = \frac{4}{9}\frac{\alpha^3\omega^3}{2I+1}\left|\sum_{n_-}\frac{\langle f\|D\|n_-\rangle\langle F,n_-\|V_{\mathrm{hf}}\|F,i\rangle}{E_{n_-}-E_i}\right|^2. \tag{30}$$

Here, $\omega=E_i-E_f$ is the energy of the emitted photon, and as before, the states $|n_-\rangle$ have odd parity and $J=1$. The electric-quadrupole term in $V_{\mathrm{hf}}$ does not play a role, for it couples ${}^3P_0^o$ to states with $J=2$. These, however, cannot decay to the ground state via $E1$ one-photon emission. We use the abbreviated notation $|F,n\rangle$ in the reduced matrix elements of $V_{\mathrm{hf}}$ in Eq. (30) to indicate that these states are angular-momentum coupled states of the entire atom with total angular momentum $F$.

The ${}^3P_0^o$ decay rates in the fermionic alkaline-earth-metal isotopes, as calculated on the basis of Eq. (30), are collected in Table II. We note that the lifetimes are now much shorter—by about ten orders of magnitude—than in the bosonic isotopes. Nevertheless, this is still sufficiently long to make the ${}^1S_0 \rightarrow {}^3P_0^o$ transition interesting for optical atomic clocks. Especially the strontium isotope ${}^{87}$Sr—which has a rather narrow ${}^3P_0^o$ linewidth of about 1 mHz—is a candidate for a future ultraprecise atomic clock [16]. The results of other calculations [59–61] are also shown in Table II. For ${}^{25}$Mg, our rate is larger by a factor of two than the rate quoted in Refs. [59,61]. The agreement is better for ${}^{43}$Ca and ${}^{87}$Sr. Pal'chikov [60] obtained a ${}^3P_0^o$ decay rate of $5.5\times10^{-3}$ s$^{-1}$ in ${}^{87}$Sr. This is somewhat smaller than our result (and the result by Porsev and Derevianko [61]), apparently for two reasons. First, we have used experimental excitation energies, and second, we have included a larger number of intermediate states when evaluating Eq. (30). If we apply the same restrictions as Pal'chikov, we find $6\times10^{-3}$ s$^{-1}$ in ${}^{87}$Sr.

### B. ${}^3P_1^o$

The ${}^3P_1^o$ state can decay via two obvious decay modes. On one hand, $M1$ one-photon decay from the ${}^3P_1^o$ to the ${}^3P_0^o$ state can take place. This mode, however, is slower by many orders of magnitude than the $E1$ decay directly to the ${}^1S_0$ ground state. The only reason the ${}^3P_1^o$ state is metastable is the necessity of a spin flip. The $E1$ decay is enabled by the presence of spin-orbit coupling—a relativistic effect that becomes more pronounced in heavier atoms.

The $E1$ decay rate is given by [56]

$$\Gamma_{\mathrm{E1}} = \frac{4}{3}\frac{\alpha^3\omega^3}{2J_i+1}|\langle f\|D\|i\rangle|^2. \tag{31}$$

Our calculated reduced electric-dipole matrix elements for the ${}^3P_1^o \rightarrow {}^1S_0$ transition agree to about the 10% level with recent high-level many-body and configuration-interaction calculations [62,63]. The result for the calculated decay rate, $\Gamma_{\mathrm{E1}}$, is presented in Table III. As expected, the decay rate increases from Mg to Sr due to enhanced spin-orbit coupling.

TABLE III. Spontaneous decay rate, in s$^{-1}$, of the ${}^3P_1^o$ state in the alkaline-earth-metal atoms magnesium ($3s3p$), calcium ($4s4p$), and strontium ($5s5p$). The decay is dominated by the $E1$ rate for the transition ${}^3P_1^o \rightarrow {}^1S_0$.

| Mg | Ca | Sr |
|---|---|---|
| $3.6(1)\times10^2$ | $2.1(2)\times10^3$ | $4.1(4)\times10^4$ |

The ${}^3P_1^o$ decay rate in all three alkaline-earth-metal atoms is sufficiently large to allow their direct experimental determination. The most recent measurements give $1.9(3)\times10^2$ s$^{-1}$ for Mg [64], $2.9(2)\times10^3$ s$^{-1}$ for Ca [65], and $4.7(1)\times10^4$ s$^{-1}$ for Sr [65]. Perfect agreement is not expected for our simple model approach. Nonetheless, we may conclude that our calculated reduced electric-dipole matrix elements are apparently accurate to about the 10% level.

### C. ${}^3P_2^o$

Alkaline-earth-metal atoms in the ${}^3P_0^o$ state do not possess a magnetic-dipole moment. In the ${}^3P_1^o$ state they do, but even in Mg this state decays after about 5 ms. The third candidate, ${}^3P_2^o$, is the only one useful for magnetic trapping [66], due to its inherently long lifetime [27].

There are several different modes through which the ${}^3P_2^o$ state can decay. Transitions within the ${}^3P^o$ fine-structure manifold are mediated by parity-conserving one-photon operators. The rate associated with a magnetic-dipole transition to the ${}^3P_1^o$ state can be written as [56]

$$\Gamma_{M1} = \frac{4}{3}\frac{\alpha^3\omega^3}{2J_i+1}|\langle f\|M_1\|i\rangle|^2. \tag{32}$$

While it is permissible to neglect magnetic-octupole decay, the electric-quadrupole decay to the ${}^3P_1^o$ state must be taken into consideration. The rate for the latter process is given by [56]

$$\Gamma_{\mathrm{E2}} = \frac{1}{15}\frac{\alpha^5\omega^5}{2J_i+1}|\langle f\|Q\|i\rangle|^2, \tag{33}$$

where

$$Q_q = -\sum_i r_i^2 C_{2,q}(\vartheta_i,\varphi_i). \tag{34}$$

The $E2$ mechanism also allows for decay from ${}^3P_2^o$ to ${}^3P_0^o$. Finally, direct decay to the ${}^1S_0$ ground state requires a parity-changing one-photon operator of rank 2, i.e., the magnetic-quadrupole operator [67,68]

$$M_{2,q} = -\sqrt{6}\alpha\sum_i r_i\left\{[\boldsymbol{C}_1(\vartheta_i,\varphi_i)\otimes\boldsymbol{s}_i]_{2,q} + \frac{1}{3}[\boldsymbol{C}_1(\vartheta_i,\varphi_i)\otimes\boldsymbol{l}_i]_{2,q}\right\}. \tag{35}$$

The associated rate is [56]

TABLE IV. Spontaneous decay rates, in $\mathrm{s}^{-1}$, of the $^3P_2^o$ state in the alkaline-earth-metal atoms magnesium ($3s3p$), calcium ($4s4p$), and strontium ($5s5p$).

| Transition | Type | Mg | Ca | Sr |
|---|---|---|---|---|
| $^3P_2^o \rightarrow {}^3P_1^o$ | $M1$ | $1(1)\times 10^{-6}$ | $1.6(3)\times 10^{-5}$ | $8(2)\times 10^{-4}$ |
| $^3P_2^o \rightarrow {}^3P_1^o$ | $E2$ | $1(3)\times 10^{-12}$ | $3(1)\times 10^{-10}$ | $3(1)\times 10^{-7}$ |
| $^3P_2^o \rightarrow {}^3P_0^o$ | $E2$ | $0(1)\times 10^{-11}$ | $9(3)\times 10^{-10}$ | $9(4)\times 10^{-7}$ |
| $^3P_2^o \rightarrow {}^1S_0$ | $M2$ | $4.2(2)\times 10^{-4}$ | $1.1(1)\times 10^{-4}$ | $1.1(2)\times 10^{-4}$ |
| Total rate | | $4.2(2)\times 10^{-4}$ | $1.3(1)\times 10^{-4}$ | $9(2)\times 10^{-4}$ |
| Ref. [27] | | $4.42\times 10^{-4}$ | $1.41\times 10^{-4}$ | $9.55\times 10^{-4}$ |

$$\Gamma_{M2} = \frac{1}{15}\frac{\alpha^5\omega^5}{2J_i+1}|\langle f\|M_2\|i\rangle|^2. \tag{36}$$

Our calculated decay rates are shown in Table IV. We see that in Mg and Ca, the exotic $M2$ mode dominates by far. In Sr, however, due to the $\omega^3$ dependence in Eq. (32), $M1$ decay makes the biggest contribution. Also shown in Table IV is a comparison of our calculated total rates with those determined by Derevianko, Ref. [27]. We find good agreement and conclude that the $^3P_2^o$ lifetimes in Mg, Ca, and Sr are, respectively, $2.4(1)\times 10^3$ s, $7.7(6)\times 10^3$ s, and $1.1(3)\times 10^3$ s. The first measurement, by Yasuda and Katori, of the $^3P_2^o$ lifetime in $^{88}$Sr yielded $500^{+280}_{-130}$ s [69], which is compatible with the current level of theory.

## IV. DYNAMIC STARK EFFECT

As mentioned in the Introduction, Sec. I, the transition from the ground state to the $^3P_0^o$ state in the fermionic isotope $^{87}$Sr is of interest for the development of an ultraprecise optical clock based on neutral atoms trapped in an optical lattice [14–18]. It has been pointed out by Katori *et al.* that with this approach a relative accuracy of better than $10^{-17}$ should be achievable [16].

The optical lattice serves three purposes. If each lattice site is occupied by at most one atom, collisional clock shifts can be suppressed (see Ref. [18] for a discussion of frequency shifts caused by dipole-dipole interactions among atoms in different lattice sites). Furthermore, using trapped atoms, long interaction times with the probe laser can be realized. This is particularly important when exciting a transition with exceptionally small linewidth (see Table II). A third benefit is the possibility of confining the atoms in the Lamb-Dicke regime [14,16,17,70]. In this way, atomic recoil and Doppler shifts can be eliminated.

The intense laser field needed to confine the atoms perturbs them. To lowest order in perturbation theory, each atomic level is shifted by a level-specific amount proportional to the intensity of the laser [71]. This effect is referred to as *dynamic* (or *ac*) Stark shift. The dynamic Stark shift of state $|m\rangle$ can be calculated from [71]

TABLE V. Magic wavelength, in nanometer, for the transition $(ns^2)^1S_0 \rightarrow (nsnp)^3P_0^o$. At this wavelength, the dynamic Stark shifts, Eq. (37), of both levels, $^1S_0$ and $^3P_0^o$, are identical.

| Mg | Ca | Sr |
|---|---|---|
| 470(10) | 700(50) | 770(60) |

$$\Delta E_m = \frac{2\pi}{3}\frac{\alpha\mathcal{I}}{2J_m+1} \times \sum_n \left\{ \frac{|\langle n\|D\|m\rangle|^2}{E_m - E_n - \omega} + \frac{|\langle n\|D\|m\rangle|^2}{E_m - E_n + \omega} \right\}. \tag{37}$$

In this equation, $\mathcal{I}$ is the laser intensity in units of $\mathcal{I}_0 = \alpha c e^2/a_0^4 = 6.4364\times 10^{15}$ W/cm$^2$; $\omega$ is the laser photon energy.

However, it is possible to find a *magic* wavelength for the trapping laser field such that the dynamic Stark shifts of the two levels involved in the clock transition are identical [14,16,17]. In other words, at the magic wavelength, the clock frequency is virtually unaffected by the presence of the optical lattice. In a recent calculation, the magic wavelength for the $^1S_0 \rightarrow {}^3P_0^o$ transition in Sr was found to be about 800 nm [16], in agreement with the experimental value of 813.5(9) nm [17].

Using Eq. (37), we determined the magic wavelength for the proposed clock transition within our model-potential approach. The results are collected in Table V. Within our error bars, our result for Sr is in agreement with the previous calculation and with the experiment. To our knowledge, Mg and Ca have not been considered before. As can be seen in Table V, the magic wavelength in Mg is too blue to be ideal for trapping with current laser sources. The magic wavelength we find in Ca appears to be much more attractive. In view of this result and of the small decay width of the $^3P_0^o$ state in $^{43}$Ca (see Table II), fermionic calcium appears to be an excellent candidate for an optical atomic clock and may serve as an interesting alternative to $^{87}$Sr.

## V. LONG-RANGE PARAMETERS

### A. $^1S_0$

While collisions among atoms are to be minimized in atomic clocks, interatomic interactions at temperatures close to absolute zero are highly intriguing and are responsible for some of the most interesting effects in the physics of ultracold gases [26,72–74]. In order to understand cold collisions, detailed knowledge about the long-range behavior of the interatomic interaction potential is indispensable [72]. It should be noted, however, that even though the scattering length is a sensitive function of the long-range parameters, a meaningful estimate for the scattering length can in general only be found if information about the short-range properties of the interatomic interaction potential is also available.

Here, we concentrate on the long-range interaction between two identical alkaline-earth-metal atoms in the same quantum state. If the two interacting atoms have vanishing angular momentum, $J=0$, then at the leading, second-order level of the long-range expansion of the interaction energy

TABLE VI. $C_6$ long-range dispersion coefficient, in atomic units, for two $(ns^2)^1S_0$ alkaline-earth-metal atoms.

|  | Mg | Ca | Sr |
|---|---|---|---|
| This work | 620(5) | 2150(60) | 3260(100) |
| Ref. [78] | 648 | 2042 | 3212 |
| Ref. [79] | 627(12) | 2221(15) | 3170(196) |
| Ref. [80] | 629.5 | 2188 | 3250 |

[75–77], both atoms can only become polarized—and thus reduce the overall energy of the system—by making virtual electric-dipole transitions to states with $J=1$. In this case, the electric dipole–dipole dispersion interaction energy between atoms in atomic state $|m\rangle$, separated by distance $R$, is well known to be given by the leading $-C_6/R^6$ term, where [75–77]

$$C_6 = \frac{2}{3}\sum_{n_1,n_2} \frac{|\langle n_1\|D\|m\rangle|^2 |\langle n_2\|D\|m\rangle|^2}{E_{n_1}+E_{n_2}-2E_m}. \qquad (38)$$

For $^1S_0$ atoms, the states $|n_1\rangle$, $|n_2\rangle$ have angular momentum $J=1$ and odd parity. The $C_6$ coefficients we calculated for Mg, Ca, and Sr in the atomic ground state are listed in Table VI. Our numbers can be compared with high-level *ab initio* [78,79] and semiempirical [80] data. The high quality of our results is evident, even though the excellent numerical agreement especially with Refs. [79] and [80] may be somewhat fortuitous, since, in contrast to those papers, we have not included core excitations when evaluating Eq. (38). The monotonic increase of the $C_6$ coefficient from Mg to Sr is a simple consequence of the greater polarizability of the heavier alkaline-earth-metal atoms.

### B. $^3P_0^o$

More interesting for future experiments with metastable atoms is the long-range physics of the $^3P_0^o$ state. As we have seen in Table II, in this state the lifetime, under spontaneous emission, of bosonic alkaline-earth-metal atoms is virtually unlimited. Any quenching of the metastable state will be induced by collisions with either atoms or photons. It is not clear, for example, on what timescale a gas consisting of $^3P_0^o$ atoms will disintegrate due to inelastic processes, how these processes can be controlled, or what role elastic collisions have to play. An important first step toward an answer consists again in determining the corresponding $C_6$ coefficient. For $^3P_0^o$ atoms, the states $|n_1\rangle$, $|n_2\rangle$ in Eq. (38) have angular momentum $J=1$ and even parity. The result of our calculation is shown in Table VII. As for ground state atoms, we observe a monotonic dependence of the $C_6$ coefficient on the atomic number. Additionally, it should be noted that in the $^3P_0^o$ state the $C_6$ coefficients for all three atomic species are greater than in the ground state by a factor of about 1.5. This expresses the fact that for excited atoms, the relevant energy denominators in Eq. (38) are smaller on average.

TABLE VII. $C_6$ long-range dispersion coefficient, in atomic units, for two $(nsnp)^3P_0^o$ alkaline-earth-metal atoms.

| Mg | Ca | Sr |
|---|---|---|
| 980(30) | 3020(200) | 5260(500) |

TABLE VIII. Atomic electric-quadrupole moment, in atomic units, in the $(nsnp)\ ^3P_2^o$ state.

|  | Mg | Ca | Sr |
|---|---|---|---|
| This work | 8.38 | 12.7 | 15.4 |
| Ref. [33] | 8.46(8) | 12.9(4) | 15.6(5) |
| Ref. [27] | 8.59 | 13.6 | 16.4 |

### C. $^3P_2^o$

As Derevianko pointed out [27], the very long lifetime (see Sec. III C) of alkaline-earth-metal atoms in the lowest $^3P_2^o$ state makes magnetic trapping of these metastable species experimentally practical. This expectation has turned out to be correct [29–32]. However, what ultimately limit the efficiency of evaporative cooling in a magnetic trap are inelastic collisions [35], not radiative decay processes. The strong coupling to inelastic scattering channels is caused by the anisotropic long-range interactions between the nonspherical $^3P_2^o$ atoms.

The most important parameter in this context is the atomic electric-quadrupole moment [27,34]. For an atom in state $|m\rangle$ with angular momentum $J_m$, the electric-quadrupole moment can be written as [34]

$$\mathcal{Q} = 2\sqrt{\frac{J_m(2J_m-1)}{(J_m+1)(2J_m+1)(2J_m+3)}}\langle m\|Q\|m\rangle. \qquad (39)$$

$\mathcal{Q}$ vanishes, of course, if $J_m=0$ or $J_m=1/2$. The atomic electric-quadrupole moment gives rise to direct, first-order quadrupole-quadrupole interactions proportional to $1/R^5$ [81]. Derevianko was the first to calculate $\mathcal{Q}$ for $^3P_2^o$ alkaline-earth-metal atoms [27]; improved data were published recently [33]. We list the results from Refs. [27] and [33] together with our calculated values in Table VIII. Again, our model calculations provide data of quality similar to the data derived from high-level many-body theory, Ref. [33]. The monotonic increase of $\mathcal{Q}$ with respect to atomic number reflects the increase in spatial extension of the excited *np* orbital, where $n=3$ for Mg, $n=4$ for Ca, and $n=5$ for Sr.

The electric dipole-dipole dispersion physics is also more complicated for $J=2$ than for $J=0$. We introduce *intermediate* dispersion coefficients to characterize the dispersion interaction between nonspherical atoms [34]:

$$B_{J_1J_2} = (-1)^{1+J_1-J_2}\frac{4}{9}\frac{1}{(2J_m+1)^2} \times \sum_{n_1,n_2}\frac{|\langle n_1\|D\|m\rangle|^2 |\langle n_2\|D\|m\rangle|^2}{E_{n_1}+E_{n_2}-2E_m}. \qquad (40)$$

In our specific case of two interacting $^3P_2^o$ atoms, $J_m=2$, and

TABLE IX. Intermediate dispersion coefficients for two interacting alkaline-earth-metal atoms in the $(nsnp)^3P_2^o$ state. See Eq. (40) for a definition of $B_{J_1J_2}$. The results presented in Ref. [33] have been converted using Eq. (41). All data are in atomic units.

| | Mg | Ca | Sr |
|---|---|---|---|
| $B_{1,1}$ (this work) | −35.6(2) | −81(3) | −139(7) |
| $B_{1,1}$ (Ref. [33]) | −38(4) | −92(9) | −158(16) |
| $B_{2,1}$ (this work) | 42.5(2) | 119(5) | 196(9) |
| $B_{2,1}$ (Ref. [33]) | 44(4) | 123(12) | 203(20) |
| $B_{2,2}$ (this work) | −51.9(2) | −176(8) | −280(10) |
| $B_{2,2}$ (Ref. [33]) | −52(5) | −167(17) | −264(26) |
| $B_{3,1}$ (this work) | −73.4(7) | −203(10) | −370(30) |
| $B_{3,1}$ (Ref. [33]) | −77(8) | −225(23) | −415(42) |
| $B_{3,2}$ (this work) | 88.6(7) | 302(20) | 546(50) |
| $B_{3,2}$ (Ref. [33]) | 90(9) | 306(31) | 555(56) |
| $B_{3,3}$ (this work) | −152(2) | −553(70) | −1210(200) |
| $B_{3,3}$ (Ref. [33]) | −156(16) | −600(60) | −1290(130) |

$|n_1\rangle$, $|n_2\rangle$ denote even-parity states with angular momenta $J_1$ and $J_2$, respectively. Both $J_1$ and $J_2$ can vary between 1, 2, and 3, so there are six nontrivial intermediate dispersion coefficients. They are displayed in Table IX. [The remaining three coefficients can be obtained by simple sign changes, according to Eq. (40).] Derevianko *et al.* [33] use intermediate dispersion coefficients defined as

$$C_6^{J_1J_2} = -\frac{27}{8}(2J+1)^2 B_{J_1J_2}. \tag{41}$$

Their converted *ab initio* data are also shown in Table IX. The agreement between both data sets is satisfying.

The restriction to long-range expansion terms up to $1/R^6$ is valid only for interatomic distances of the order of 100 Bohr radii or larger. In this regime, however, energies associated with rotations of the diatomic frame of an interacting pair are comparable with the interatomic interaction energies, and the coupling between the rotational and the electronic degrees of freedom induced by the anisotropic interatomic interaction must be explicitly taken into account. Reference [34] develops a tensorial theory appropriate for this purpose and shows how the parameters $\mathcal{Q}$ and $B_{J_1J_2}$ enter the theory.

## VI. CONCLUSION

In this paper, we have theoretically investigated properties of the energetically lowest $^3P^o$ manifold in the alkaline-earth-metal atoms Mg, Ca, and Sr. The latter two, in particular, are the subject of strong current interest. Using an electron-correlation approach for the valence shell in combination with a physically well-motivated potential for the valence interaction with the core shells, we have been able to reproduce existing *ab initio* data with good accuracy. This provides an independent check on a number of crucial atomic parameters for present-day experiments.

The calculations presented here also supply data that have not, to our knowledge, been presented elsewhere. First, the $E1M1$ decay rate of the $^3P_0^o$ state in spinless alkaline-earth-metal species was not previously known. The difference in level structure to heliumlike atoms may motivate a direct search for the exotic $E1M1$ decay process in heavy magnesiumlike (or berylliumlike) ions. Second, our calculation of the hyperfine-induced $E1$ decay rate of the $^3P_0^o$ state in $^{43}$Ca, and also our determination of the magic wavelength for the corresponding clock transition from the ground state of calcium, may be of interest for the development of a future generation of optical atomic clocks. Finally, we have calculated the $C_6$ dispersion coefficient describing the long-range interaction between two metastable $^3P_0^o$ alkaline-earth-metal atoms. This system, which is free from any losses due to Penning ionization, may be ideal for studying cold collisions between spherical, metastable atoms.

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[1] C. E. Moore, *Atomic Energy Levels*, Natl. Stand. Ref. Data Ser. 35 (U.S. GPO, Washington, D.C., 1971).

[2] R. Marrus and P. J. Mohr, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and B. Bederson (Academic Press, New York, 1978), Vol. 14.

[3] H. Katori, T. Ido, Y. Isoya, and M. Kuwata-Gonokami, Phys. Rev. Lett. **82**, 1116 (1999).

[4] T. Binnewies, G. Wilpers, U. Sterr, F. Riehle, J. Helmcke, T. E. Mehlstäubler, E. M. Rasel, and W. Ertmer, Phys. Rev. Lett. **87**, 123002 (2001).

[5] E. A. Curtis, C. W. Oates, and L. Hollberg, Phys. Rev. A **64**, 031403(R) (2001).

[6] J. Grünert and A. Hemmerich, Phys. Rev. A **65**, 041401(R) (2002).

[7] D. N. Madsen and J. W. Thomsen, J. Phys. B **35**, 2173 (2002).

[8] X. Xu, T. H. Loftus, M. J. Smith, J. L. Hall, A. Gallagher, and J. Ye, Phys. Rev. A **66**, 011401(R) (2002).

[9] W. C. Magno, R. L. Cavasso-Filho, and F. C. Cruz, Phys. Rev. A **67**, 043407 (2003).

[10] X. Xu, T. H. Loftus, J. W. Dunn, C. H. Greene, J. L. Hall, A. Gallagher, and J. Ye, Phys. Rev. Lett. **90**, 193002 (2003).

[11] C. W. Oates, F. Bondu, R. W. Fox, and L. Hollberg, Eur. Phys. J. D **7**, 449 (1999).

[12] Th. Udem, S. A. Diddams, K. R. Vogel, C. W. Oates, E. A.

Curtis, W. D. Lee, W. M. Itano, R. E. Drullinger, J. C. Bergquist, and L. Hollberg, Phys. Rev. Lett. **86**, 4996 (2001).

[13] G. Wilpers, T. Binnewies, C. Degenhardt, U. Sterr, J. Helmcke, and F. Riehle, Phys. Rev. Lett. **89**, 230801 (2002).

[14] T. Ido and H. Katori, Phys. Rev. Lett. **91**, 053001 (2003).

[15] I. Courtillot, A. Quessada, R. P. Kovacich, A. Brusch, D. Kolker, J.-J. Zondy, G. D. Rovera, and P. Lemonde, Phys. Rev. A **68**, 030501(R) (2003).

[16] H. Katori, M. Takamoto, V. G. Pal'chikov, and V. D. Ovsiannikov, Phys. Rev. Lett. **91**, 173005 (2003).

[17] M. Takamoto and H. Katori, Phys. Rev. Lett. **91**, 223001 (2003).

[18] D. E. Chang, J. Ye, and M. D. Lukin, Phys. Rev. A **69**, 023810 (2004).

[19] T. P. Dinneen, K. R. Vogel, E. Arimondo, J. L. Hall, and A. Gallagher, Phys. Rev. A **59**, 1216 (1999).

[20] G. Zinner, T. Binnewies, F. Riehle, and E. Tiemann, Phys. Rev. Lett. **85**, 2292 (2000).

[21] M. Machholm, P. S. Julienne, and K.-A. Suominen, Phys. Rev. A **64**, 033425 (2001).

[22] M. Machholm, P. S. Julienne, and K.-A. Suominen, Phys. Rev. A **65**, 023401 (2002).

[23] R. L. Cavasso-Filho, A. Scalabrin, D. Pereira, and F. C. Cruz, Phys. Rev. A **67**, 021402(R) (2003).

[24] E. A. Cornell and C. E. Wieman, Rev. Mod. Phys. **74**, 875 (2002).

[25] W. Ketterle, Rev. Mod. Phys. **74**, 1131 (2002).

[26] C. J. Pethick and H. Smith, *Bose-Einstein Condensation in Dilute Gases* (Cambridge University Press, Cambridge, 2002).

[27] A. Derevianko, Phys. Rev. Lett. **87**, 023002 (2001).

[28] T. Loftus, J. R. Bochinski, and T. W. Mossberg, Phys. Rev. A **66**, 013411 (2002).

[29] H. Katori, T. Ido, Y. Isoya, and M. Kuwata-Gonokami, in *Atomic Physics XVII*, edited by Ennio Arimondo, Paolo De Natale, and Massimo Inguscio, AIP Conf. Proc. No. 551 (AIP, Melville, NY, 2001).

[30] S. B. Nagel, C. E. Simien, S. Laha, P. Gupta, V. S. Ashoka, and T. C. Killian, Phys. Rev. A **67**, 011401(R) (2003).

[31] X. Xu, T. H. Loftus, J. L. Hall, A. Gallagher, and J. Ye, J. Opt. Soc. Am. B **20**, 968 (2003).

[32] D. P. Hansen, J. R. Mohr, and A. Hemmerich, Phys. Rev. A **67**, 021401(R) (2003).

[33] A. Derevianko, S. G. Porsev, S. Kotochigova, E. Tiesinga, and P. S. Julienne, Phys. Rev. Lett. **90**, 063002 (2003).

[34] R. Santra and C. H. Greene, Phys. Rev. A **67**, 062713 (2003).

[35] V. Kokoouline, R. Santra, and C. H. Greene, Phys. Rev. Lett. **90**, 253201 (2003).

[36] C. H. Greene, Phys. Rev. A **42**, 1405 (1990).

[37] C. H. Greene and M. Aymar, Phys. Rev. A **44**, 1773 (1991).

[38] M. Aymar, C. H. Greene, and E. Luc-Koenig, Rev. Mod. Phys. **68**, 1015 (1996).

[39] K. J. Bathe, *Finite Element Procedures in Engineering Analysis* (Prentice-Hall, Englewood Cliffs, NJ, 1976).

[40] K. J. Bathe and E. Wilson, *Numerical Methods in Finite Element Analysis* (Prentice-Hall, Englewood Cliffs, NJ, 1976).

[41] M. Braun, W. Schweizer, and H. Herold, Phys. Rev. A **48**, 1916 (1993).

[42] J. Ackermann and J. Shertzer, Phys. Rev. A **54**, 365 (1996).

[43] T. N. Rescigno, M. Baertschy, D. Byrum, and C. W. McCurdy, Phys. Rev. A **55**, 4253 (1997).

[44] K. W. Meyer, C. H. Greene, and B. D. Esry, Phys. Rev. Lett. **78**, 4902 (1997).

[45] G. H. Golub and C. F. Van Loan, *Matrix Computations* (Johns Hopkins University Press, Baltimore, 1996).

[46] R. B. Lehoucq, D. C. Sorensen, and C. Yang, *ARPACK Users' Guide: Solution of Large-Scale Eigenvalue Problems with Implicitly Restarted Arnoldi Methods* (Society for Industrial and Applied Mathematics, Philadelphia, 1998).

[47] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1998).

[48] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 1957).

[49] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press, New York, 1959).

[50] R. N. Zare, *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics* (Wiley, New York, 1988).

[51] G. W. F. Drake, Nucl. Instrum. Methods Phys. Res. B **9**, 465 (1985).

[52] I. M. Savukov and W. R. Johnson, Phys. Rev. A **66**, 062507 (2002).

[53] L. N. Labzowsky and A. V. Shonin, Phys. Rev. A **69**, 012503 (2004).

[54] D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Dover, Mineola, NY, 1998).

[55] Nuclear data were extracted from the Evaluated Nuclear Structure Data File database (http://www.nndc.bnl.gov/nndc/ensdf/) maintained by the National Nuclear Data Center at Brookhaven National Laboratory.

[56] I. I. Sobelman, *Atomic Spectra and Radiative Transitions* (Springer-Verlag, Berlin, 1992).

[57] G. zu Putlitz, Z. Phys. **175**, 543 (1963).

[58] S. M. Heider and G. O. Brink, Phys. Rev. A **16**, 1371 (1977).

[59] R. G. Garstang, J. Opt. Soc. Am. **52**, 845 (1962).

[60] V. G. Pal'chikov, in Proceedings of the European Frequency and Time Forum EFTF 2002 (St. Petersburg, Russia, 2002) (unpublished).

[61] S. G. Porsev and A. Derevianko, e-print physics/0312006.

[62] S. G. Porsev, M. G. Kozlov, Yu. G. Rakhlina, and A. Derevianko, Phys. Rev. A **64**, 012508 (2001).

[63] I. M. Savukov and W. R. Johnson, Phys. Rev. A **65**, 042503 (2002).

[64] A. Godone and C. Novero, Phys. Rev. A **45**, 1717 (1992).

[65] R. Drozdowski, M. Ignaciuk, J. Kwela, and J. Heldt, Z. Phys. D: At., Mol. Clusters **41**, 125 (1997).

[66] T. Bergeman, G. Erez, and H. J. Metcalf, Phys. Rev. A **35**, 1535 (1987).

[67] M. Mizushima, Phys. Rev. **134**, A883 (1964).

[68] R. H. Garstang, Astrophys. J. **148**, 579 (1967).

[69] M. Yasuda and H. Katori, e-print physics/0310074.

[70] R. H. Dicke, Phys. Rev. **89**, 472 (1953).

[71] M. H. Mittleman, *Introduction to the Theory of Laser–Atom Interactions* (Plenum Press, New York, 1993).

[72] J. Weiner, V. S. Bagnato, S. Zilio, and P. S. Julienne, Rev. Mod. Phys. **71**, 1 (1999).

[73] F. Dalfovo, S. Giorgini, L. P. Pitaevskii, and S. Stringari, Rev. Mod. Phys. **71**, 463 (1999).

[74] A. J. Leggett, Rev. Mod. Phys. **73**, 307 (2001).

[75] H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

[76] A. Dalgarno and W. D. Davison, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann

(Academic Press, New York, 1966), Vol. 2.

[77] T. Y. Chang, Rev. Mod. Phys. **39**, 911 (1967).

[78] J. F. Stanton, Phys. Rev. A **49**, 1698 (1994).

[79] S. G. Porsev and A. Derevianko, Phys. Rev. A **65**, 020701(R) (2002).

[80] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **68**, 052714 (2003).

[81] J. K. Knipp, Phys. Rev. **53**, 734 (1938).