

Properties of the triplet metastable states of the alkaline-earth-metal atoms

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The static and dynamic properties of the alkaline-earth-metal atoms in their metastable state are computed in a configuration interaction approach with a semiempirical model potential for the core. Among the properties determined are the scalar and tensor polarizabilities, the quadrupole moment, some of the oscillator strengths, and the dispersion coefficients of the van der Waals interaction. A simple method for including the effect of the core on the dispersion parameters is described.

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I. INTRODUCTION

The low-lying triplet metastable states of alkaline-earth-metal atoms have been generating increasing interest in the area of cold-atom physics for a number of reasons. One application is to use the $^1S_0^e \rightarrow ^3P_1^o$ transition in calcium as a new optical frequency standard [1]. The use of the $^1S_0^e \rightarrow ^3P_0^o$ transitions for fermionic ^{87}Sr stored in an optical lattice is expected to further result in an improved standard [2]. Another possible application is in the formation of Bose-Einstein condensates (BEC) consisting of alkaline-earth-metal atoms [3,4] in their metastable triplet states. The stability, size and excitation modes of BECs depends on the sign (and magnitude) of the scattering length, and the scattering length depends sensitively on the precise values of the dispersion constants [5,6].

Taken in conjunction, the desirability of obtaining precise values of the static and dynamic properties of the low-lying $nsnp\ ^3P^o$ metastable state has greatly increased in importance. In this article, properties of these states are computed from valence electron configuration interaction calculations that use a semiempirical model potential to describe the core-valence interaction [7–11]. Among the data computed are the oscillator strengths for some of the low-lying transitions, the scalar and tensor polarizabilities, the quadrupole moments, and the dispersion coefficients for the van der Waals interaction between two atoms.

II. RESULTS OF THE CALCULATIONS

A. Methodology

The properties of these states are computed using configuration interaction (CI) calculations that treat the correlations between the valence particles in an *ab initio* manner while using a semiempirical model potential to describe the core-valence interaction [7–11]. The details of this calculation are very similar to those reported in [9,11,12] apart from some minor changes in the cutoff parameters and the use of an orbital basis of larger dimension. The polarization potentials were initially defined by tuning the potential to reproduce the

ns , np , nd and nf binding energies of the respective singly ionized atom. The Hamiltonian was then diagonalized in a basis consisting of all the two-electron basis states that could be formed from a set of about 140–150 single particle orbitals. The basis set contained orbitals up to and including $\ell \leq 8$ and the two-electron basis dimensions ranged from 1000 to 4000. For all practical purposes the basis for the two-valence electrons can be regarded as saturated. The initial binding energies obtained by this procedure were not in perfect agreement with experiment with discrepancies for the ground and excited state energies of the order of 0.1–2.0 % (refer to [9,12] to get an indication of the accuracy). Some further tuning of the cutoff parameters was done to improve the accuracy of the energy differences which directly impact on the accuracy of expectation values. Expectation values for multipole operators were computed with a modified operator that allowed for polarization corrections [11,13,14].

The model potential is quite realistic since the direct and exchange interactions with the core were computed without approximation from a Hartree-Fock (HF) wave function, only the core polarization potential was described with a model potential. The resulting polarizabilities, and dispersion parameters for homonuclear pairs of atoms were generally within 0.1% of the best variational calculations for Li or Be, and for heavier atoms they were generally within 1–2 % of results coming from large fully relativistic calculations combining configuration interaction and many-body perturbation theory techniques [11].

The most likely source of error in the present calculations for the heavier species, Ca and Sr, is the neglect of relativistic effects. However, the use of a polarization potential tuned to the experimental binding energy will implicitly take into account the influence of relativistic effects upon the core electron distribution. Further, Greene and Aymar have shown that the spin-orbit interaction does not have major effect on the structure of the alkaline-earth-metal wave functions [15].

B. Energy levels

The energy levels of the present calculations are given in Table I and compared with experiment. The polarization cutoff parameters were fine-tuned to reproduce the experimental binding energy of the lowest states of each symmetry. In the case for states with $L > 0$ the parameters were tuned to reproduce the center-of-gravity of the spin-orbit triplets. The

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TABLE I. Theoretical and experimental energy levels (in Hartree) of some of the low-lying metastable states of the alkaline-earth-metal atoms. The energies are given relative to the energy of the doubly ionized core. The experimental energies for the triplet states are averages with the usual $(2J+1)$ weighting factors. The experimental data are taken from [16,17]. The md level is the $3d$ level for Be, Mg, and Ca while for Sr it is the $4d$ level.

Systems Level	Be		Mg		Ca		Sr	
	Theory	Expt.	Theory	Expt.	Theory	Expt.	Theory	Expt.
$ns^2\ ^1S^e$	-1.011842	-1.011850	-0.833533	-0.833530	-0.660944	-0.660932	-0.614598	-0.614602
$nsnp\ ^3P^o$	-0.911710	-0.911701	-0.733378	-0.733788	-0.591387	-0.591388	-0.547611	-0.547612
$ns(n+1)s\ ^3S^e$	-0.774561	-0.774552	-0.645827	-0.645821	-0.517230	-0.517228	-0.482289	-0.482292
$np^2\ ^3P^e$	-0.739862	-0.739855	-0.569906	-0.569929	-0.485477	-0.485478	-0.452720	-0.452717
$nsmd\ ^3D^e$	-0.729118	-0.729113	-0.615041	-0.615022	-0.568193	-0.568180	-0.531359	-0.531367

spin-orbit splitting of the triplet states is largest for strontium and its magnitude is about 0.001 Hartree.

The agreement between the theoretical and experimental energy levels is sufficiently close to discount the possibility that energy level considerations might make a significant contribution to the uncertainty in the oscillator strengths and polarizabilities.

C. Quadrupole moments

The quadrupole moment of the $^3P_2^o$ state is a static property of the state. An exact knowledge of its value is important since the quadrupole-quadrupole interaction has a big impact of the cold collision physics in metastable alkaline-earth metal atoms [4,18]. Defining the LS coupled reduced matrix element as

$$Q(L) = \langle \Psi(^3P^o) | \sum_i r_i^2 C^2(\hat{\mathbf{r}}_i) | \Psi(^3P^o) \rangle, \quad (1)$$

the quadrupole moment for a triplet state is usually defined as the moment of $^3P_J^o$ state with $M_J=J$. In the expression above $C^2(\hat{\mathbf{r}})$ is the spherical tensor of rank 2. The quadrupole moment is defined as

$$Q = \left\langle \Psi(^3P_J^o); M_J=J \left| \sum_i r_i^2 C_0^2(\mathbf{r}_i) \right| \Psi(^3P_J^o); M_J=J \right\rangle. \quad (2)$$

This can be written [19]

$$Q = \sqrt{\frac{4J(2J-1)}{(J+1)(2J+1)(2J+3)}} (2J+1)(-1)^{2+S+L+J} \times \begin{Bmatrix} S & L & J \\ 2 & J & L \end{Bmatrix} Q(L), \quad (3)$$

where the Wigner-Eckart theorem has been used twice to collapse the angular factors. The quadrupole moment for a 3P level is often given for the $J=2$ state. The quadrupole moment Q for the $J=2$ state is equal to $2\langle Q_{zz} \rangle$.

Some older calculations of $\langle Q_{zz} \rangle$ exist [20,21]. The finite element multiconfiguration Hartree-Fock (MCHF) calculation of Sundholm and Olsen for Be gave 4.53 a.u. which is in excellent agreement with the present value of 4.54 a.u. The CI calculations of Ceraulo and Berry [20] consistently under-

estimated the present quadrupole moments (e.g., 7.944 a.u. for Mg) and are not listed in Table II.

The quadrupole moments are compared with the recent calculations by other groups in Table II. The CI+MBPT calculation [4] is a fully relativistic calculation with the post-HF interactions between the valence electrons and the core treated with perturbation theory while the interaction between the two valence electrons are treated with the CI ansatz.

The calculation of Santra and Greene [22] (SG-CI) treated the two active electrons within a CI framework while using a model potential to represent the core-valence interaction. The model potential did include a spin-orbit interaction. One limitation with the SG-CI calculation is that it does not include the dielectronic part of the polarization potential.

The noticeable feature of Table II is that all three calculations agree with each other with a total variation of less than 2%. The present results generally lie closer to the CI+MBPT calculation than the SG-CI calculation. The high level of agreement between three completely independent calculations suggests that the uncertainty ascribed by Derevanko *et al.* to their quadrupole moment was too big by a factor of 2.

D. Oscillator strengths of low-lying transitions

The oscillator strengths for the transitions to the lowest lying $^3S^e$, $^3P^e$ and $^3D^e$ states are given in Table II. The absorption oscillator strength from state ψ_0 is calculated according to the identity

$$f_{0n} = \frac{2|\langle \psi_0; L_0 S | \sum_i r_i C^1(\hat{\mathbf{r}}_i) | \psi_n; L_n S \rangle|^2 \epsilon_{0n}}{3(2L_0+1)}. \quad (4)$$

The oscillator strengths for the Be triplet transitions are probably as accurate as any that have previously been published. The basis for the valence electrons is effectively saturated and the semiempirical approach to core polarization is capable of high accuracy [11]. For example, the present methodology reproduces the dipole and quadrupole polarizability of Be given by a close to exact calculation [23] to an accuracy of 0.2%. The present oscillator strengths agree very well with the experimental values given in Table II. Not shown in

TABLE II. Properties of the metastable ${}^3P^o$ levels of the alkaline-earth-metal atoms and He (note the lowest ${}^3P^o$ level is not metastable in He). The oscillator strengths to the lowest ${}^3S^e$, ${}^3P^e$, and ${}^3D^e$ states are given as $f({}^3L^e)$. The scalar and tensor dipole polarizabilities are α_0 and α_{2,L_0L_0} , respectively. The quadrupole moment Q is given for the ${}^3P_2^o$ state while the dispersion parameter C_6 is that for two ${}^3P_0^o$ states. The He ‘‘Other Theory’’ row reports the results of close to exact calculations with the exception of α_{2,L_0L_0} . The present oscillator strength to the He ${}^3D^e$ state is not to a physical state, rather it is to the lowest energy pseudostate. All quantities are in atomic units and the numbers in brackets are the uncertainties in the last digits.

Method	$f({}^3S^e)$	$f({}^3P^e)$	$f({}^3D^e)$	Q	α_0	α_{2,L_0L_0}	C_6
He							
Present	-0.1797		0.6251	10.264	46.66	69.62	5102
Other Theory	-0.1797 [33]		0.6102 [33]	10.265 [34]	46.71 [35]	67.09 [36]	
Be							
Present	0.08187	0.4467	0.2948	4.54	39.02	0.558	220.3
MCHF [37]					39.33	0.47	
TDGI [38]	0.026		0.154		36.08	1.04	
<i>B</i> -spline CI [39]	0.0823	0.453	0.295				
Experiment	0.089(3) [40]	0.44(2) [41]	0.29(1) [40]				
Mg							
Present	0.1383	0.6167	0.6287	8.44	101.9	-14.24	1004
CI+MBPT [4]				8.46(8)			
SG-CI [22]				8.38			980(30)
TDGI [42]	0.136		0.625		90.7	-19.64	
MS-CI [27]	0.1354	0.6383	0.6336				
Experimental	0.139(3) [26]	0.55(4) [43]	0.62(4) [44]				
Ca							
Present	0.1582	0.5071	0.08136	12.96	295.3	-28.36	3363
CI+MBPT [4]				12.9(4)			
SG-CI [22]				12.7			3020(200)
TDGI [45]	0.163		0.051		276	-50.0	
CI+model [28]	0.1526	0.5030	0.0873				
MCHF [29]	0.161	0.525	0.0806				
Experimental	0.12(2) [46]	0.522(13) [47]					
Sr							
Present	0.1788	0.4727	0.08254	15.51	494.8	-53.84	6074
CI+MBPT [4]				15.6(5)			
SG-CI [22]				15.4			5260(500)
MQDT [30]	0.173		0.0849				
Experimental	0.188(10) [48]	0.438(4) [31]					

the table are the ${}^3P^o \rightarrow {}^3P^e$ oscillator strengths of CI calculation of Weiss [24] and the MCHF calculation of Jonsson *et al.* [25]. Both of these calculations were very large and incorporated both core and valence excitations. The Weiss f -value was 0.447, while the Jonsson *et al.* result was 0.4463. These could hardly be any closer to the present value of 0.4467.

The present oscillator strength for the transition to the ${}^3S^e$ state in Mg, namely 0.138 is in excellent agreement with that obtained from the low uncertainty experiment of Andra *et al.* [26], 0.139 ± 0.003 . Agreement with the large basis CI calculation of Moccia and Spizzo (MS-CI) is also good [27]. The MS-CI calculation is similar to the present calculation in that excitations are only permitted for the valence electrons. It does not allow for core-valence correlations so the present approach, which does, should be regarded as being more reliable.

In the case of Ca, good agreement is achieved with the model potential calculations of Hansen *et al.* [28] for the

transitions to the ${}^3S^e$ and ${}^3P^e$ states. A 7% discrepancy occurs for the transition of the $4s3d {}^3D^e$ state. The larger difference here is expected since the $3d$ orbital does have a tendency to penetrate into the core and therefore degrade the accuracy associated with model potential methods. The best *ab initio* calculation is the MCHF calculation by Froese-Fischer and Tachiev [29]. The MCHF calculation allows for core-valence correlations and also includes relativistic effects using the Breit-Pauli Hamiltonian. The MCHF oscillator strengths listed in Table II are a weighted average of the individual lines in the multiplet. The largest difference between the present and MCHF oscillator strengths is less than 4%.

The multichannel quantum defect theory (MQDT) calculations of Werji *et al.* [30] which use an *R*-matrix calculation to determine the short-range parameters. Their transition rate data was converted to oscillator strengths using experimental energy differences and lie within 2–3 % of the present oscillator strengths.

The most precise experiment for Sr is that of Andra *et al.* [31] which gave a lifetime of 7.89 ± 0.05 ns for the $5p^2 \ ^3P_2^e$ state. This state can decay to the both the $5s5p$ and $5s6p$ levels and the lifetime was converted to an oscillator strength by neglecting the transition to the $5s6p$ state. This assumption is justified since the dipole matrix element will be small due to the $\langle 5p|6p \rangle$ overlap, and the $5s6p^2 \ ^3P^o \rightarrow 5p^2 \ ^3P^e$ energy difference of 0.0073 Hartree is also small.

The comparison with the time-dependent gauge independent (TDGI) calculations of Merewa *et al.* [32] is mainly of interest because these authors also give estimates of the scalar and tensor polarizabilities. A quick comparison of TDGI f -values with other results in Table II reveals that their oscillator strengths do not have the same level of accuracy as the other calculations. The underlying atomic structure information entering the TDGI formalism comes from CI calculations.

E. The polarizabilities

1. Theoretical treatment of polarizabilities

This analysis is done under the premise that spin-orbit effects are small and the radial parts of the wave functions are the same for the states with different J .

The Stark energy shifts for the different L_0 levels in an electric field F are written as [49]

$$\Delta E = -\frac{1}{2} \alpha_{L_0 M_0} F^2. \quad (5)$$

The Stark shifts for the different M_0 states of the $^3P^o$ level are different and the polarizability is written as

$$\alpha_{L_0 M_0} = \alpha_0 + \frac{3M_0^2 - L_0(L_0 + 1)}{L_0(2L_0 - 1)} \alpha_2. \quad (6)$$

where α_2 is taken from the state with $M_0 = L_0$. The total polarizability is written in terms of both a scalar and tensor polarizability. The scalar polarizability represents the average shift of the different M levels while the tensor polarizability gives the differential shift.

In terms of second order perturbation theory, the energy shift from an electric field, F pointing in the z direction is

$$\Delta E = \frac{1}{2} \sum_n \frac{2 \langle \psi_0; L_0 M_0 | \sum_i r_i C_0^1(\hat{\mathbf{r}}_i) | \psi_n; L_n M_n \rangle \langle \psi_n; L_n M_n | \sum_i r_i C_0^1(\hat{\mathbf{r}}_i) | \psi_0; L_0 M_0 \rangle F^2}{(E_0 - E_n)}. \quad (7)$$

The polarizability can therefore be written

$$\alpha_{L_0 M_0} = \sum_n \begin{pmatrix} L_0 & 1 & L_n \\ -M_0 & 0 & M_n \end{pmatrix}^2 \frac{2 |\langle \psi_0; L_0 | \sum_i r_i C^1(\hat{\mathbf{r}}_i) | \psi_n; L_n \rangle|^2}{(E_0 - E_n)}, \quad (8)$$

where the Wigner-Eckart theorem has been used to isolate the M -dependent terms. Using the definition of the oscillator strength, Eq. (4), and taking the average of the energy shifts leads to the usual definition as a sum rule over the oscillator strengths. It is

$$\alpha_0 = \sum_{M_0=-L_0}^{L_0} \alpha_{L_0 M_0} / (2L_0 + 1) = \sum_n \frac{f_{0n}}{\epsilon_{0n}^2}, \quad (9)$$

where the sum includes both valence and core excitations and $\epsilon_{0n} = (E_0 - E_n)$. The f -value distribution for the core was estimated using a semiempirical method [11]. In this approach one writes

$$\alpha_{core} = \sum_{i \in core} \frac{N_i}{(\epsilon_i + \Delta)^2}, \quad (10)$$

where N_i is the number of electrons in a core orbital, ϵ_i is the Koopman energy, and Δ is an energy shift parameter chosen

so that Eq. (10) reproduces an accurate estimate of the core polarizability determined by other, independent means.

Since the M -dependent part of the polarizability is a tensor of rank 2 and it is easiest to define it in terms of $\alpha_{2, L_0 L_0}$,

$$\alpha_{2, L_0 M_0} = \alpha_{2, L_0 L_0} \times (-1)^{L_0 - M_0} \begin{pmatrix} L_0 & 2 & L_0 \\ -M_0 & 0 & M_0 \end{pmatrix} / \begin{pmatrix} L_0 & 2 & L_0 \\ -L_0 & 0 & L_0 \end{pmatrix} \quad (11)$$

$$= \alpha_{2, L_0 L_0} \frac{3M_0^2 - L_0(L_0 + 1)}{L_0(2L_0 - 1)}, \quad (12)$$

where $\alpha_{2, L_0 L_0}$ is

$$\alpha_{2, L_0 L_0} = \sum_n \left[\begin{pmatrix} L_0 & 1 & L_n \\ -L_0 & 0 & L_0 \end{pmatrix}^2 - \frac{1}{3(2L_0 + 1)} \right] \times \frac{2 |\langle \psi_0; L_0 | \sum_i r_i C^1(\hat{\mathbf{r}}_i) | \psi_n; L_n \rangle|^2}{(E_0 - E_n)}. \quad (13)$$

In terms of an f -value sum, this reduces to

$$\alpha_{2,L_0L_0} = - \left(\sum_{n,L_n=0} \frac{f_{0n}}{\epsilon_{0n}^2} - \frac{1}{2} \sum_{n,L_n=1} \frac{f_{0n}}{\epsilon_{0n}^2} + \frac{1}{10} \sum_{n,L_n=2} \frac{f_{0n}}{\epsilon_{0n}^2} \right). \quad (14)$$

The core does not make a contribution to the tensor polarizability since it has an equal impact on all the different M -levels.

The development above is for LS coupled states, but it is common to give the tensor polarizability for LSJ states. These can be related to the LS states by geometric factors arising from the application of Racah algebra. The polarizability can be expanded

$$\alpha_{J_0M_0} = \alpha_0 + \frac{3M_0^2 - J_0(J_0 + 1)}{J_0(J_0 - 1)} \alpha_{2,J_0J_0}, \quad (15)$$

where α_{2,J_0J_0} is the tensor polarizability of the state with $M_0=J_0$. The scalar polarizability for the different J levels are the same and equal to the scalar polarizability in the L representation. The tensor polarizability between the L and J representations can be related by

$$\alpha_{2,J_0J_0} = \alpha_{2,L_0L_0} (2J_0 + 1) (-1)^{S+L_0+J_0+2} \begin{Bmatrix} S & L_0 & J_0 \\ 2 & J_0 & L_0 \end{Bmatrix} \times \frac{\begin{pmatrix} J_0 & 2 & J_0 \\ -J_0 & 0 & J_0 \end{pmatrix}}{\begin{pmatrix} L_0 & 2 & L_0 \\ -L_0 & 0 & L_0 \end{pmatrix}}. \quad (16)$$

When $J=1$ this reduces to $\alpha_{2,J_0J_0} = -\alpha_{2,L_0L_0}/2$. (This result has been checked by converting our LS coupled f -values into LSJ coupled values and then using the standard expression in terms of the $|\langle J_0 || \mathbf{r} || J_n \rangle|^2$ matrix elements [49].)

2. Results of calculations

The program logic and associated numerics were initially tested by estimating the polarizabilities of the $1s2p \ ^3P^o$ level of He. The present α_0 of $46.66 a_0^3$ is within 0.12% of the close to exact calculation of Yan *et al.* [35]. Agreement with the TDGI α_{2,L_0L_0} of Rerat and Pouchan [36] is not as good, but it should be noted that the TDGI calculation obtains an α_0 of $49.5 a_0^3$, indicating that the Rerat-Pouchan calculation is not quite converged.

The present estimates of the Be polarizabilities are the most accurate that have been published. The agreement with the Themelis and Nicolaides MCHF calculation [37] for α_0 is reasonable, but they give an α_{2,L_0L_0} that is about 20% smaller. This level of agreement is acceptable given that the MCHF calculation was much smaller, the $2s2p \ ^3P^o$ state was represented by a 3 configuration MCHF wave function while 14 configurations were used to represent the excited states.

Only a moderate level of agreement is achieved with the TDGI polarizabilities for Be, Mg and Ca [38,42,45]. The static polarizabilities agree at the 10% level while the TDGI estimates of the tensor polarizability are up to 50% different. The lower level of accuracy achieved by the TDGI calculations is consistent with the earlier discussion concerning the accuracy of the oscillator strengths.

A recent measurement of the tensor polarizability for the $^3P_1^o$ state of Ca using an atomic polarization interferometer gave $2.623 \pm 0.015 \text{ kHz}/(\text{kV}/\text{cm})^2$ or $10.54 \pm 0.06 a_0^3$ [50]. The tensor polarizability of the $J=1$ state is determined from the Ca entry in Table II by multiplying by $-\frac{1}{2}$ according to Eq. (16). The present calculation gives $\alpha_{2,J_0J_0} = 14.2 a_0^3$ for the $^3P_1^o$ state. A very early estimate of the tensor polarizability for this state was $12.9 \pm 3.2 a_0^3$ [51] and another independent experiment gave $\alpha_{2,J_0J_0} = 12.1 \pm 0.8 a_0^3$ [52].

The scalar polarizability of the $^3P^o$ state has not been measured directly, but there have been measurements of the difference between the polarizabilities of the $4s^2 \ ^1S_0^e$ ground state and the $^3P_1^o (m=0)$ ground state. Morinaga *et al.* [53] obtained $90.4 \pm 13.5 a_0^3$ for the difference in the polarizabilities. Using the polarizability of $159.4 a_0^3$ for the Ca ground state [11], and the present $^3P_1^o (m=0)$ polarizability of $295.3 - 2 \times 14.2 = 266.9 a_0^3$ gives $107.5 a_0^3$ for the difference in the polarizability.

The Stark frequency shift of Li and van Wijngaarden of $12.314 \pm 0.041 \text{ kHz}/(\text{kV}/\text{cm})^2$ for the $4s^2 \ ^1S_0^e \rightarrow ^3P_1^o (m=0)$ transition [54] converts to a polarizability difference of $98.98 \pm 0.33 a_0^3$.

Taken together, present estimates of α_{2,J_0J_0} are larger than experiment by about 20% while estimates of the $\alpha_0(4s^2 \ ^1S_0^e) - \alpha_0(4s4p \ ^3P_1^o)$ polarizability difference are about 10% too large. Rectifying the situation in a nonrelativistic calculation could be problematic since an improvement in α_{2,J_0J_0} will result in the theoretical polarizability difference drifting further away from the experimental polarizability difference.

The obvious improvement that could eliminate this problem would be the inclusion of the spin-orbit interaction. The largest contribution to the polarizability comes from the transitions to the $^3D^e$ levels. The spin-orbit splitting leads to the excitation energies for $4s3d$ states with differing J fluctuating by about $\pm 2\%$. Given the cancellations that occur in the evaluation of Eq. (13) it is possible that introduction of spin-orbit splitting could lead to a Ca tensor polarizability in better agreement with experiment.

There have been no measurements of the tensor polarizability for the other alkaline-earth-metal atoms. This should be rectified since it would be a very useful diagnostic with which to assess the accuracy of the structure models of the metastable states.

3. Alternate treatment of core

It is desirable to partition the core f -value some into contributions that arise from excitations to final states with different core+valence angular momentum, L_T . Therefore, it is possible to write symbolically

$$\alpha_{core} = \sum_{L_T} \alpha_{core,L_T}, \quad (17)$$

where α_{core,L_T} will include all the contributions from the different magnetic sublevels, i.e.,

$$\alpha_{core,L_T} = \sum_{M_T} \alpha_{core,L_T M_T}. \quad (18)$$

For any of the core dipole excited magnetic sublevels one can write

$$\alpha_{core,L_T M_T} = \sum_n \frac{f(00:LM \rightarrow n; L_T M_T)}{\epsilon_{0n}^2}. \quad (19)$$

The final states, $|L_T M_T\rangle$ can be expanded in terms of uncoupled states, e.g.,

$$|L_T M_T\rangle = \sum_{mM} \langle 1mLM | L_T M_T \rangle |1mLM\rangle, \quad (20)$$

where $1m$ refers to the angular momentum of the excited core and LM refers to the angular momentum of the ${}^3P^o$ metastable state which is acting as a spectator. Therefore, it is possible to decompose the oscillator strength as

$$f(0;00LM \rightarrow n; L_T M_T) = \sum_{mM} |\langle 1mLM | L_T M_T \rangle \langle L_T M_T \rangle|^2 \times f(0;00LM \rightarrow n; 1mLM). \quad (21)$$

The polarizability can also be expanded in terms of uncoupled states

$$\alpha_{L_T M_T} = \sum_{mM} |\langle 1mLM | L_T M_T \rangle \langle L_T M_T \rangle|^2 \alpha_{core,mM} / (2L+1). \quad (22)$$

The factor of $(2L+1)$ in the denominator arises due to the sum over spectator states. We now assume that the excitations for the core occur independently of the state of valence electrons which act as spectators. Therefore, the contribution to the polarizability is independent of M . Further, the core initially has a net angular momentum of zero and therefore the different magnetic sublevels of the core excitations should give equal contributions to the polarizability, hence

$$\alpha_{core,mM} = \frac{\alpha_{core}}{3}. \quad (23)$$

The final result is

$$\alpha_{L_T M_T} = \sum_{mM} |\langle 1mLM | L_T M_T \rangle \langle L_T M_T \rangle|^2 \frac{\alpha_{core}}{3(2L+1)}, \quad (24)$$

which can be simplified by summing the Clebsch-Gordan coefficients to give

$$\alpha_{core,L_T} = \frac{(2L_T+1)\alpha_{core}}{3(2L+1)}. \quad (25)$$

When particular values are substituted into Eq. (25) the distribution of the core f -value sum into the ${}^3S^o$, ${}^3P^o$ and ${}^3D^o$ manifolds is given in the proportion $\frac{1}{9} : \frac{3}{9} : \frac{5}{9}$. This is of course just the statistical weighting associated with the $(2L_T+1)$ degeneracy factor. It is simple to verify that such a proportion means the net contribution of the core to the tensor polarizability as defined by Eq. (14) is zero.

F. The van der Waals coefficients

The van der Waals coefficients given in Table II are those for a pair of ${}^3P_0^o$ states. The dispersion parameter, C_6 is simple to compute since both of the atoms have a net angular momentum of zero. The expression is

$$C_6 = \frac{3}{2} \sum_{n_1, n_2} \frac{f_{0,n_1} f_{0,n_2}}{\epsilon_{0n_1} \epsilon_{0n_2} (\epsilon_{0n_1} + \epsilon_{0n_2})}. \quad (26)$$

The present dispersion parameters are slightly larger than those of the SG-CI calculation of Santra and Greene [22]. Taking the case of Sr, the difference here is about 15%. About half of this difference can be attributed to the core since $C_6 = 5668$ a.u. when core excitations are omitted from Eq. (26). So part of the discrepancy arises from the neglect of the core in the SG-CI calculation. One cautionary note should be made. Santra and Greene reported C_6 for the ${}^3P_0^o$ state. Since the ${}^3P_0^o$ state is the most tightly bound state of the $5s5p$ multiplet one expects the present LS coupled calculation to have a slightly larger C_6 . The quantitative impact of spin-orbit splitting can best be determined by separate evaluations of C_6 for the $J=0, 1$ and 2 states.

The van der Waals coefficients that are relevant to BEC studies are those between two ${}^3P_2^o$ states. The algebra related to this is somewhat messy and the coefficients are presented in the formalism of Santra and Greene [19,22]. The intermediate dispersion coefficient between two ${}^3P_J^o$ states is defined as

$$B_{J_1 J_2} = (-1)^{J_1 - J_2 + 1} \sum_{n_1, n_2} \frac{f_{0,n_1} f_{0,n_2}}{\epsilon_{0n_1} \epsilon_{0n_2} (\epsilon_{0n_1} + \epsilon_{0n_2})}, \quad (27)$$

where n_1 has angular momentum J_1 and n_2 has angular momentum J_2 .

This LS coupled oscillator strengths were converted into the LSJ coupling scheme using the identity

$$f(J_0 \rightarrow J_n) = f(L_0 \rightarrow L_n) (2L_0+1)(2J_n+1) \begin{Bmatrix} S & L_0 & J_0 \\ 1 & J_n & L_n \end{Bmatrix}^2. \quad (28)$$

When the sum, Eq. (27), was evaluated, the core f -value distribution was included using Eq. (25) to partition it into ${}^3S^e$, ${}^3P^e$ and ${}^3D^e$ excitations.

The results of our calculations are presented in Table III and compared with earlier CI+MBPT calculations of Der-evianko *et al.* [4] and the SG-CI calculations [22]. There is no apparent experimental activity on the metastable states of Be and the present data in the table were only included for reasons of completeness.

The present calculation and the CI+MBPT calculation could hardly be in any better agreement for magnesium. The largest disagreement for any of the B_{J_1, J_2} coefficients was 1.2% for the $B_{2,2}$ coefficient. Agreement with the SG-CI calculation is not as good with the occasional discrepancy of 5% and it is noticeable that the present and CI+MBPT results do tend to be larger in magnitude.

TABLE III. The intermediate dispersion coefficients, $B_{J_1 J_2}$ for two alkaline-earth-metal atoms in the metastable $^3P_2^o$ state. The $\sum |B_{J_i J_j}|$ column sums the absolute value of all the entries in each row (with off-diagonal elements added twice). The numbers in brackets after the data are the uncertainties ascribed to the CI+MBPT and SG-CI calculations.

Method	$B_{1,1}$	$B_{2,1}$	$B_{2,2}$	$B_{3,1}$	$B_{3,2}$	$B_{3,3}$	$\sum B_{J_i J_j} $
Be							
Present	-6.901	11.29	-27.77	-13.52	22.31	-27.21	220.3
Mg							
Present	-37.46	43.90	-52.73	-76.49	90.76	-157.2	1004
CI+MBPT [4]	-37.8(38)	43.9(44)	-52.1(52)	-76.7(77)	90.1(90)	-156.4(156)	1002
SG-CI [22]	-35.6(2)	42.5(2)	-51.9(2)	-73.4(7)	88.6(7)	-152(2)	976
Ca							
Present	-96.95	130.7	-176.8	-233.5	317.5	-604.8	3363
CI+MBPT [4]	-91.7(92)	123(12)	-167(17)	-225(23)	306(31)	-600(60)	3250
SG-CI [22]	-81(3)	119(5)	-176(8)	-203(10)	302(20)	-553(70)	3087
Sr							
Present	-165.9	213.9	-278.9	-416.9	556.0	-1231	6074
CI+MBPT [4]	-158(16)	203(20)	-264(26)	-415(42)	555(56)	-1290(130)	6090
SG-CI [22]	-139(7)	196(9)	-280(10)	-370(30)	546(50)	-1210(200)	5780

For calcium there is a tendency for the present results to be from 1% to 5% larger in magnitude with the differences being smaller for the larger values of J_1 and J_2 . The present dispersion coefficients all lie within the 10% uncertainty that Derevianko *et al.* associate with their results. Agreement with the SG-CI calculations is not so good with discrepancies exceeding 10% being common.

The pattern for strontium is similar to that seen for calcium. The present $B_{J_1 J_2}$ coefficients are larger than the CI+MBPT data for $B_{1,1}$ and smaller for $B_{3,3}$. The differences with the SG-CI calculation are generally larger than those with the CI+MBPT calculation.

Some general trends are noticeable. The SG-CI calculation always gave the smallest result for $B_{1,1}$, $B_{2,1}$, $B_{3,1}$, $B_{3,2}$ and $B_{3,3}$. Furthermore, the sum $\sum_{J_i J_j} B_{J_i J_j}$ for the present calculations and CI+MBPT calculations are consistently bigger than the SG-CI calculations, with the difference becoming larger as the atom gets heavier. This could be a manifestation of the increasing importance of the core contribution to the $B_{J_i J_j}$ coefficients as the atom gets heavier.

It is also evident that some of the uncertainty estimates of the SG-CI calculation were somewhat optimistic. For example, they give $B_{1,1} = 139 \pm 7$ a.u. for strontium. The contribution of the core f -value sum to this dispersion parameter is 12.0 a.u. So the core contribution, which is not incorporated in the SG-CI calculation, is larger than their estimated uncertainty.

III. CONCLUSIONS

A systematic study of the properties of the alkaline-earth-metal atoms reveals that the present nonrelativistic approach reproduces the results of the CI+MBPT ansatz of Derevianko *et al.* [4] to better than 5%. Agreement with the model potential CI calculation of Santra and Greene [22] is not so good with discrepancies of 10–15 % occurring for the spherical part of the C_6 dispersion coefficient. Due to the unknown

impact of the spin-orbit energy, splitting upon the polarizabilities and dispersion coefficients, it is not possible to make a definitive statement about any reasons for the differing levels of agreement with these two other calculations. However, we do suspect that the omissions of the SG-CI model, i.e., the dielectronic two body polarization potential, the non-usage of a dressed dipole transition operator, and the lack of core excitation terms in the dispersion sum rules all contribute in part to the differences with the SG-CI model.

It should be noted that previous studies with the present model for the alkali-metal atoms and singlet states of the alkaline atoms demonstrated that the method could predict a number of expectation values with an overall accuracy of 1–2 % or better [11]. The presence of spin-orbit energy splitting, and the existence of a $^3D^e$ state very close in energy to the $^3P^o$ metastable level leads to a decrease in accuracy for atomic properties such as the tensor polarizability that are sensitive to these energy differences. Additional high precision measurements of the tensor polarizabilities for the Mg, Ca and Sr would certainly be worthwhile since the sensitivity of this parameter to the fine details of the wave function should help in the refinement of the two-body potentials used to characterize ultracold collisions.

It is interesting to speculate whether the better agreement with the CI+MBPT calculations could be achieved by incorporating a spin-orbit potential into the Hamiltonian and using jj coupling. Alternatively, a fully relativistic treatment, using a relativistic HF wave function might be necessary. Resolution of these questions requires that explicit calculations be made to determine the additional physics needed to eliminate the anomalies between the present calculations and experiment and between the present calculations and the CI+MBPT calculations.

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- [1] G. Wilpers, T. E. Binnewies, C. Degenhardt, U. Sterr, J. Helmcke, and F. Riehle, *Phys. Rev. Lett.* **89**, 230801 (2002).
- [2] H. Katori, M. Takamoto, V. G. Pal'chikov, and V. D. Ovsianikov, *Phys. Rev. Lett.* **91**, 173005 (2003).
- [3] A. Derevianko, J. F. Babb, and A. Dalgarno, *Phys. Rev. A* **63**, 052704 (2001).
- [4] A. Derevianko, S. G. Porsev, S. Kotochigova, E. Tiesinga, and P. S. Julienne, *Phys. Rev. Lett.* **90**, 063002 (2003).
- [5] E. Tiesinga, S. Kotochigova, and P. S. Julienne, *Phys. Rev. A* **65**, 042722 (2002).
- [6] E. Timmermans, R. Cote, and I. Simbotin, *J. Phys. B* **33**, 4157 (2000).
- [7] J. Mitroy, D. C. Griffin, D. W. Norcross, and M. S. Pindzola, *Phys. Rev. A* **38**, 3339 (1988).
- [8] J. Mitroy, *J. Phys. B* **26**, 2201 (1993).
- [9] M. W. J. Bromley and J. Mitroy, *Phys. Rev. A* **65**, 062505 (2002).
- [10] J. Mitroy and M. W. J. Bromley, *Phys. Rev. A* **68**, 035201 (2003).
- [11] J. Mitroy and M. W. J. Bromley, *Phys. Rev. A* **68**, 052714 (2003).
- [12] M. W. J. Bromley and J. Mitroy, *Phys. Rev. A* **65**, 012505 (2002).
- [13] S. Hameed, A. Herzenberg, and M. G. James, *J. Phys. B* **1**, 822 (1968).
- [14] S. Hameed, *J. Phys. B* **5**, 746 (1972).
- [15] C. H. Greene and M. Aymar, *Phys. Rev. A* **44**, 1773 (1991).
- [16] nist, NIST Atomic Spectra Database Version 2.0 (2001), URL: <http://physics.nist.gov/cgi-bin/AtData/main.asd>.
- [17] C. E. Moore, *Atomic Energy Levels* (Molybdenum-Actinium, NSRDS-NBS 35) (US GPO, Washington, DC, 1971), Vol. 3.
- [18] V. Kokoouline, R. Santra, and C. H. Greene, *Phys. Rev. Lett.* **90**, 253201 (2003).
- [19] R. Santra and C. H. Greene, *Phys. Rev. A* **67**, 062713 (2003).
- [20] S. C. Ceraulo and R. S. Berry, *Phys. Rev. A* **44**, 4145 (1991).
- [21] D. Sundholm and J. Olsen, *Phys. Rev. A* **47**, 2672 (1993).
- [22] R. Santra, K. V. Christ, and C. H. Greene, *Phys. Rev. A* **69**, 042510 (2004).
- [23] J. Komasa, *Phys. Rev. A* **65**, 012506 (2002).
- [24] A. W. Weiss, *Phys. Rev. A* **51**, 1067 (1995).
- [25] P. Jönson, C. Froese Fischer, and P. Godefroid, *J. Phys. B* **32**, 1233 (1999).
- [26] H. J. Andra, in *Progress in Atomic Spectroscopy, Part B*, edited by W. Hanle and H. Klein-poppen (Plenum, New York, 1979), Chap. 20, p. 829.
- [27] R. Moccia and P. Spizzo, *J. Phys. B* **21**, 1133 (1988).
- [28] J. E. Hansen, C. Laughlin, H. W. van der Hart, and G. Verbockhaven, *J. Phys. B* **32**, 2099 (1999).
- [29] C. F. Fischer and G. Tachiev, *Phys. Rev. A* **68**, 012507 (2003).
- [30] H. G. C. Werjji, C. H. Greene, C. E. Theodosiou, and A. Gallagher, *Phys. Rev. A* **46**, 1248 (1992).
- [31] H. J. Andrä, H. Plöhn, W. Wittmann, A. Gaupp, J. O. Stoner, and M. Gaillard, *J. Opt. Soc. Am.* **65**, 1410 (1975).
- [32] D. Begue, M. Merewa, M. Rerat, and C. Pouchan, *Chem. Phys. Lett.* **301**, 43 (1999).
- [33] G. W. F. Drake, *Handbook of Atomic, Molecular and Optical Physics* (American Institute of Physics, Woodbury, 1996).
- [34] Z. C. Yan and G. W. F. Drake, *Phys. Rev. A* **50**, R1980 (1994).
- [35] Z. C. Yan, J. M. Zhu, and B. L. Zhou, *Phys. Rev. A* **62**, 034501 (2000).
- [36] M. Rerat and C. Pouchan, *Phys. Rev. A* **49**, 829 (1994).
- [37] S. I. Themelis and C. A. Nicolaides, *Phys. Rev. A* **52**, 2439 (1995).
- [38] D. Begue, M. Merawa, M. Rerat, and C. Pouchan, *J. Phys. B* **31**, 5077 (1998).
- [39] M. K. Chen, *J. Phys. B* **31**, 4523 (1998).
- [40] J. Bromander, *Phys. Scr.* **4**, 61 (1971).
- [41] T. Andersen, J. R. Roberts, and G. Sorensen, *Phys. Scr.* **4**, 52 (1971).
- [42] M. Merawa, D. Begue, M. Rerat, and C. Pouchan, *Chem. Phys. Lett.* **334**, 403 (2001).
- [43] L. Lundin, B. Engman, J. Hilke, and I. Martinson, *Phys. Scr.* **8**, 274 (1973).
- [44] M. Kwiatkowski, U. Teppner, and P. Zimmermann, *Z. Phys. A* **294**, 109 (1980).
- [45] M. Merawa, C. Tendero, and M. Rerat, *Chem. Phys. Lett.* **343**, 397 (2001).
- [46] H. Kostin, *Z. Phys.* **178**, 200 (1964).
- [47] G. Smith, *J. Phys. B* **21**, 2827 (1988).
- [48] M. D. Havey, L. C. Balling, and J. J. Wright, *J. Opt. Soc. Am.* **67**, 488 (1977).
- [49] J. R. P. Angel and P. G. H. Sandars, *Proc. R. Soc. London, Ser. A* **305**, 125 (1968).
- [50] S. Yanagimachi, M. Kijuro, M. Machiya, and A. Morinaga, *Phys. Rev. A* **65**, 042104 (2002).
- [51] G. von Oppen, *Z. Phys.* **232**, 473 (1970).
- [52] K. Zeiske, G. Zinner, F. Riehle, and J. Helmcke, *Appl. Phys. B: Lasers Opt.* **60**, 205 (1995).
- [53] A. Morinaga, M. Nakamura, T. Kurosu, and N. Ito, *Phys. Rev. A* **54**, R21 (1996).
- [54] J. Li and W. A. van Wijngaarden, *Phys. Rev. A* **53**, 604 (1996).