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Long range interactions of the Mg$^+$ and Ca$^+$ ions

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Abstract. The polarizabilities of the low lying states of the Mg$^+$ and Ca$^+$ ions are evaluated by diagonalizing the semi-empirical Hamiltonians in a large dimension single electron basis. The quadrupole moment of the metastable $3d$ state Ca$^+$ is also calculated and is within 1% of a recent experimental value while being 5% smaller than some large ab-initio calculations. In addition, the long range dispersion coefficients for these ions interacting with a number of atoms are given. Oscillator strengths are also given and generally agree with the most sophisticated ab-initio calculations. The polarizabilities and dispersion coefficients can be used to estimate the frequency shifts of the Ca$^+$ $4s \rightarrow 3d$ clock transition due to background electric fields and also collisions with a buffer gas.

PACS. 34.20.Cf Interatomic potentials and forces – 31.50.-x Potential energy surfaces – 32.10.Dk Electric and magnetic moments, polarizabilities

1 Introduction

This paper gives a systematic presentation of the long range properties of the Mg$^+$ and Ca$^+$ ions, largely motivated by the importance of these ions in a number of application areas. In the case of Ca$^+$, the interest lies in astrophysics and cold ion physics. First, the absorption spectrum of the Ca$^+$ ion is used to explore the structure and properties of interstellar dust clouds [1,2]. Second, the long lifetime of the $4s \rightarrow 3d$ transition of the Ca$^+$ ion make it a promising candidate for a trapped ion frequency standard [3–7]. In addition, the long lifetime of the $3d$ state makes it well suited for storing and processing quantum information [4,8–10]. Finally, there have been a number of investigations of pressure broadening of the Ca$^+$ transitions in a variety of buffer gases [11–20]. Knowledge of the long range part of the ion-atom interaction is useful in determining the pressure broadening and shift [21,22].

The relevance of Mg$^+$ mainly comes from astrophysics since it is abundant in the interstellar medium and is one of the most common metals in interstellar dust [23,24]. One of the reasons for its importance is that magnesium is found mainly in its singly ionized form in the interstellar medium. There has also been pressure broadening research [14–17,19,20,25] and Mg$^+$ is one of the few ions to have had a direct determination of its dipole polarizability [26,27].

In the present work, one-electron models of the Mg$^+$ and Ca$^+$ ions are constructed with a semi-empirical core potential to describe the interaction of the valence electron with the rest of the atom. The polarizabilities and dispersion coefficients are evaluated using sum rules [28]. All quantities are reported in atomic units, with the exception of lifetimes and decay rates which are stated in SI units.

2 Theoretical development

2.1 Overview of dispersion constant calculations

The long range interaction between one electrically charged atom and one electrically neutral atom has two components [29–31]. First of all there is the polarization interaction, which can be written

$$V(R) = -\frac{\alpha_d}{2R^4} - \frac{\alpha_q}{2R^6} - \cdots \quad (1)$$

where α_d and α_q are the dipole and quadrupole polarizabilities of the neutral atom. The distance between the two nuclei is R. This part of the long range interaction does not lead to a frequency shift between the different states of the ion.

In addition to this, there is the dispersion interaction. For two spherically symmetric atoms in their ground states, this interaction can be written [32,33],

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots \quad (2)$$

The C_n parameters are the dispersion coefficients. The dispersion interaction does lead to a frequency shift between the ion states when the ion is immersed in a buffer gas.

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The approach used to generate the dispersion coefficients [28] is based on the work of Dalgarno who derived expressions in terms of oscillator strength sum rules [32,33]. This reduced the calculation of the C_n parameters for two spherically symmetric atoms to summations over the products of the absorption oscillator strengths (originating in the ground state) divided by an energy denominator. The sums should include contributions from all discrete and continuum excitations. In practice a pseudo-state representation is used which gives a discrete representation of the continuum [28,34,35]. Finite dimension sums over a pseudo-state basis provide a rapidly convergent expansion of the continuum of intermediate states provided all the pseudo-states are retained [36–38]. The sum over oscillator strengths needs to be rewritten in terms of a sum over the reduced matrix elements of the electric multipole operator in cases where one (or both) of the atoms is in a state with $L > 0$ [28].

The major part of any calculation involves the generation of the lists of reduced transition matrix elements for the two atomic states. In the present approach this is done by diagonalizing a semi-empirical model potential in a large single electron basis. This gives the spectrum of low lying physical states as well as the discretization of the positive energy continuum. It is then a relatively straightforward calculation to use the procedure outlined previously [28] to process the lists of matrix elements and generate the dispersion coefficients.

2.2 Wave functions and transition operators for Mg$^+$ and Ca$^+$

The wave functions and transition operators computed in this paper were obtained by diagonalizing the semi-empirical Hamiltonian [35,39–42] in a large mixed Laguerre type orbital (LTO) and Slater type orbital (STO) basis set [35].

The initial step was to perform a Hartree-Fock (HF) calculation to define the core. In this case, calculations of the Mg $3s^2$ and Ca $4s^2$ ground states were done in a STO basis [43]. The core wave functions were then frozen. The neutral atom ground state as opposed to the ion ground state was chosen to define the core for reasons of calculational convenience. Previous work by one of the authors (JM) has looked at the structure of Mg and Ca [35,44], as well as their positronic ions [45–47]. The core potentials used in these previous works (which were defined by reference to the spectra of the ionic spectrum) are used in the present calculations. The effective Hamiltonian for the valence electron is

$$H = -\frac{1}{2}\nabla^2 + V_{\rm dir}(\mathbf{r}) + V_{\rm exc}(\mathbf{r}) + V_{\rm p}(\mathbf{r}). \qquad (3)$$

The direct and exchange interactions of the valence electron with the HF core were calculated exactly. The ℓ-dependent polarization potential, $V_{\rm p}$, was semi-empirical in nature with the functional form

$$V_{\rm p}(r) = -\sum_{\ell m} \frac{\alpha_d g_\ell^2(r)}{2r^4} |\ell m\rangle\langle \ell m|. \qquad (4)$$

The coefficient, α_d is the static dipole polarizability of the core and $g_\ell^2(r) = 1 - \exp\bigl(-r^6/\rho_\ell^6\bigr)$ is a cutoff function designed to make the polarization potential finite at the origin. The cutoff parameters, ρ_ℓ were tuned to reproduce the binding energies of the ns ground state and the np, nd and nf excited states. The dipole polarizabilities were $\alpha_d = 0.4814\ a_0^3$ for Mg^{2+} [35,48] and $\alpha_d = 3.16\ a_0^3$ for Ca^{2+} [35,48,49]. The Mg^{2+} cutoff parameters for $\ell = 0 \to 3$ were 1.1795, 1.302, 1.442 and 1.520 a_0 respectively. The Ca^{2+} cutoff parameters for $\ell = 0 \to 3$ were 1.6516, 1.6594, 1.9316 and 1.77 a_0 respectively. The energies of the states with $\ell \geq 1$ were assigned to the statistical average of their respective spin-orbit doublets. The Hamiltonian was diagonalized in a very large orbital basis with about 50 Laguerre type orbitals for each ℓ-value. Although the wave functions are constructed as linear combinations of LTOS, all matrix element evaluations were done using Gaussian quadratures and are accurate to close to machine precision. The cutoff parameters were different for each $\ell \leq 3$. The parameters for $\ell > 3$ were set to ρ_3.

The oscillator strengths (and other multipole expectation values) were computed with operators that included polarization corrections [35,40,50–52]. The quadrupole core polarizability was chosen as 0.5184 a_0^5 for Mg^{2+} [35,53] and 6.936 a_0^5 for Ca^{2+} [35,53] while the octupole polarizability was set to zero. The cutoff parameter for the polarization corrections to transition operator was fixed at 1.361 a_0 (the average of ρ_0, ρ_1, ρ_2 and ρ_3) for Mg$^+$ and 1.75 a_0 (the average of ρ_0, ρ_1 and ρ_2) for Ca$^+$.

The model potential is quite realistic since the direct and exchange interactions with the core were computed without approximation from the HF wave function, and only the core polarization potential is described with a model potential. Comparisons with more sophisticated ab-initio methods have revealed that the present semi-empirical approach often gives oscillator strengths, polarizabilities and dispersion coefficients that lie within a couple of percent of the best calculations [35,54–56]. There is one complication. The $3d$ orbital of Ca$^+$ is quite compact and does penetrate into the core [49,57]. Defining the polarization potential by tuning to the $3d$ energy leads to the rest of the nd series being slightly under-bound, and then there is the issue of the accuracy of the $3d$ state itself. Consequently, quantities which explicitly involve the Ca$^+$ nd set of states can be expected to have larger uncertainties than the other states.

2.3 Wave functions and transition operators for other atoms

The atoms for which the Mg$^+$ and Ca$^+$ interactions are determined are the hydrogen atom and the rare gases. The transition data for hydrogen were taken from a pseudo-state representation of the hydrogen spectrum [35,58–60] that was generated by diagonalizing a basis of 15 Laguerre Type Orbitals. The data for helium were taken from a pseudo-state representation but in this case the underlying basis was a Hylleraas basis capable of giving close to

Table 1. Theoretical and experimental energy levels (in hartree) of some of the low-lying states of the Mg$^+$ and Ca$^+$ ions. The energies are given relative to the energy of the Mg^{2+} and Ca^{2+} cores. The experimental energies (taken from [62,63]) for the doublet states are averages with the usual $(2J+1)$ weighting factors.

State	Theory	Experimental
	Mg$^+$	
$3s$	−0.552535	−0.552536
$3p$	−0.389737	−0.389736
$4s$	−0.234324	−0.234481
$3d$	−0.226804	−0.226801
$4p$	−0.185014	−0.185114
$5s$	−0.129667	−0.129751
$4d$	−0.127373	−0.127381
	Ca$^+$	
$4s$	−0.436287	−0.436278
$3d$	−0.373921	−0.373917
$4p$	−0.320844	−0.320820
$5s$	−0.198293	−0.198588
$4d$	−0.175144	−0.177426
$5p$	−0.160060	−0.160230
$4f$	−0.126189	−0.126188

exact energies and polarizabilities for the low lying states of helium [28,61].

The pseudo-oscillator strength distributions for the heavier rare gases came from two sources. The dipole transition data were taken from the compilation of Kumar and Meath [64,65] which use high quality experimental data such as refractive index information to constrain the distribution. The distributions of Mitroy and Zhang [55] are used for the quadrupole and octupole transitions. These data initially use a distribution based on HF expectation values. This HF distribution was then refined by adjusting the excitation energies to give agreement with sophisticated calculations of the polarizabilities and dispersion constants [66,67].

3 Results

3.1 The Mg$^+$ energy levels

The binding energies of the low lying states of the Mg$^+$ are tabulated and compared with experiment in Table 1. The agreement between the present energies and the experimental energies is good with the largest discrepancy being 1.5×10^{-4} Hartree.

3.2 The Ca$^+$ energy levels

The binding energies of the low lying states of the Ca$^+$ are tabulated and compared with experiment in Table 1. The agreement between the present energies and the experimental energies is generally of order 10^{-4} Hartree with the exception of the $4d$ level where there is a discrepancy of 2.3×10^{-3} Hartree. The value of ρ_2 is set to the $3d$ energy which penetrates into the core [39,49,52,57]. Tuning the cutoff parameter to the $3d$ level leads to the binding energy of the $4d$ and higher nd levels being underestimated [39,49].

3.3 Mg$^+$ oscillator strengths

The absorption oscillator strength of multipole k for a transition from $n_a \to n_b$, with an energy difference of $\Delta E_{n_b n_a} = E_{n_b} - E_{n_a}$, is defined as

$$f^{(k)}_{n_a n_b} = \frac{2|\langle \psi_{n_a}; L_a \parallel r^k \mathbf{C}^k(\hat{\mathbf{r}}) \parallel \psi_{n_b}; L_b \rangle|^2 \Delta E_{n_b n_a}}{(2k+1)(2L_a+1)}. \quad (5)$$

Table 2 lists the present oscillator strengths for a number of Mg$^+$ transitions. Values from three other calculations are also listed [24,69,70]. These include the extensive sets of data from the coupled cluster with single and double excitations (CCSD) [24] and the data from the extensive compilation of Froese-Fischer et al. [69]. The Froese-Fischer calculation is a B-spline configuration interaction (CI) which incorporates the Breit interaction in the final diagonalization (relativistic CI). Finally, there is the large CI calculation that aimed to get an accurate oscillator strength for the weak $3s \to 4p$ transition [70].

The overall level of agreement of the present calculation with the large scale ab-initio calculations could hardly be better. For many transitions there is agreement at the 1% level or better.

The $3s \to 4p$ oscillator strength is known to be particularly difficult to determine [23,82]. From the theoretical perspective, there are significant cancellations in the radial matrix element which make the oscillator strength particularly susceptible to small changes in the calculation details. Such is the level of uncertainty for this transition that the present oscillator strength can be regarded as having the same reliability as the ab-initio calculations. Indeed, the present oscillator strength of 9.21×10^{-4} is closer to the most recent experimental value of $9.71(32) \times 10^{-4}$ [23] than two of the ab-initio calculations.

The electric quadrupole oscillator strength for the $3s \to 3d$ transition is also given in Table 2. Also given is the oscillator strength derived from line strengths of the relativistic coupled cluster calculation with single and double excitations (RCCSD) of Majumder et al. [72] (this oscillator strength was computed with the energy difference of the present calculation). This demonstrates that the present semi-empirical method is capable of giving accurate oscillator strengths for quadrupole transitions.

3.4 Ca$^+$ oscillator strengths

Table 2 lists the oscillator strengths for a number of transitions between the low lying states. Although the lifetime for the $4p$ level has been measured on numerous occasions [83,84], it is not possible to directly determine the

Table 2. Absorption oscillator strengths for various transitions of Mg^+ and Ca^+. All of the oscillator strengths are for dipole transitions with three exceptions. Theoretical oscillator strengths from other groups are identified by an acronym denoting the type of calculation and a citation. In one instance, an oscillator strength is taken from a National Institute of Standards and Technology (NIST) compilation [68]. Experimental oscillator strengths are denoted as Exp. The numbers in the square brackets denote powers of ten.

Transition	Present	Other
		Mg^+
${f^{(1)}}_{3s\to 3p}$	0.9121	0.920 RCI [69], 0.913 CCSD [24], 0.922 CI [70], 0.914(8) Exp. [71]
${f^{(1)}}_{3s\to 4p}$	9.21[−4]	7.01[−4] RCI [69], 9.31[−4] CCSD [24], 8.33[−4] CI [70], 9.71(32)[−4] Exp [23]
${f^{(1)}}_{3p\to 4s}$	0.1495	0.1495 RCI [69], 0.1456 CCSD [24]
${f^{(1)}}_{3p\to 3d}$	0.9405	0.948 RCI [69], 0.937 CCSD [24]
${f^{(1)}}_{4s\to 4p}$	1.3929	1.396 RCI [69], 1.3970 CCSD [24]
${f^{(1)}}_{3d\to 4p}$	0.1790	0.1801 RCI [69], 0.1811 CCSD [24]
${f^{(2)}}_{3s\to 3d}$	15.88	15.70 RCCSD [72],
		Ca^+
${f^{(1)}}_{4s\to 4p}$	0.9606	0.977 MCHF [52], 0.965 MBPT [73], 0.950 MBPT [74], 0.9523 MP [75], 0.970 MBPT [76]
${f^{(1)}}_{4s\to 5p}$	0.00172	0.00033 MP [75], 0.00139 MBPT [76]
${f^{(1)}}_{3d\to 4p}$	0.0660	0.0646 MCHF [77], 0.0574 MP [75], 0.064 MBPT [74], 0.0600 MBPT [73], 0.0648 MBPT [76]
${f^{(1)}}_{3d\to 5p}$	0.00038	0.00070 MP [75]
${f^{(1)}}_{3d\to 4f}$	0.1599	0.185 NIST [68], 0.1539 MBPT [76]
${f^{(1)}}_{4p\to 5s}$	0.1792	0.168 MP [75]
${f^{(1)}}_{4p\to 4d}$	0.8685	0.871 MP [75]
${f^{(2)}}_{4s\to 3d}$	2.036	2.02 MCHF [52], 1.897 MBPT [6], 1.938 MBPT [74], 2.12 [78]
${f^{(2)}}_{4s\to 4d}$	20.25	

resonant $4s \to 4p$ oscillator strength from this information since the $4p$ level can decay into both the $3d$ and $4s$ levels. Accordingly, we have converted the present oscillator strengths listed in Table 2 into a $4p$ lifetime of 6.80×10^{-9} s for comparison with experiment. The two most recent experiments give $6.89(2) \times 10^{-9}$ s [84] and $6.94(7) \times 10^{-9}$ [83] which are 1–2% larger than the present value (note, these are the statistical weights of the spin-orbit doublets). This suggests that present estimate of the resonant oscillator strength, $f_{4s\to 4p}$ is too large by 1–2%. This level of accuracy is about the same as that achieved by the three many body perturbation theory (MBPT) calculations [73,74,76] and the multi configuration Hartree-Fock (MCHF) calculation [52]. The most recent MBPT calculation by Arora et al. [76] is the most interesting since it also reported polarizabilities for the $4s$ and $3d$ levels.

The relative scatter between the different calculations of the $3d \to 4p$ oscillator strength cover a range of 15%. In absolute terms the differences are not large with a variation of 0.01 between the largest and smallest oscillator strengths. It should be noted that Arora et al. MBPT calculation is for the transition originating from the $3d_{5/2}$ level. The branching ratio of 17.6 ± 2.0 for the $4p \to 4s$ and $4s \to 3d$ decays measured by Gallagher [85] can be used to estimate an experimental oscillator strength of 0.052 ± 0.006 for the $3d \to 4p$ transition (note, this estimate of the oscillator strength is 2% smaller than previous estimates due to the use of newer estimates of the $4p$ lifetime). A more precise experimental measurement of the branching ratio would allow increased accuracy in the determination of the $3d \to 4p$ oscillator strength.

The transition rate for the $4s \to 3d$ transition has been the subject of many recent investigations [6]. The electric-quadrupole reduced matrix element for the $4s_{1/2} \to 3d_{3/2}$ transition has been determined by a MBPT calculation to be 7.934 while the reduced matrix element for the $4s_{1/2} \to 3d_{5/2}$ transition has been determined to be 9.74 [6]. The MBPT matrix elements can be converted to LS coupled matrix elements by multiplying by $\sqrt{6/5}$ and $\sqrt{4/5}$ respectively to give 8.691 and 8.720. Averaging the two values and using the statistical average of the $4s \to 3d$ energy difference gives an oscillator strength of $f^{(2)}_{4s\to 3d} = 1.897$. The current oscillator strength of 2.036 would appear to be too big by 6%.

The decay rate of an LS coupled state decaying by a quadrupole transition is given by the identity [86]

$$A^{E2} = \frac{1.120 \times 10^{18}}{(2L_b+1)\lambda^5} |\langle \psi_{n_a}; L_a \parallel r^k \mathbf{C}^k(\hat{\mathbf{r}}) \parallel \psi_{n_b}; L_b \rangle|^2. \quad (6)$$

where λ is given in angstroms. The decay rates from the MBPT calculation [6] were $A^{E2}_{3/2} = 0.8361\ \mathrm{s}^{-1}$ and $A^{E2}_{5/2} = 0.8584\ \mathrm{s}^{-1}$. The most recent experiment gave $A^{E2}_{3/2} = 0.8503(8)\ \mathrm{s}^{-1}$ and $A^{E2}_{5/2} = 0.8562(7)\ \mathrm{s}^{-1}$ [6]. These experimental values are consistent with a number of earlier experiments [6]. The present calculation using the theoretical energy difference gives $A^{E2} = 0.8780\ \mathrm{s}^{-1}$. An independent model potential calculation using much the same approach as used here reported a transition probability of $0.85\ \mathrm{s}^{-1}$ [52]. Converting this to an oscillator strength gave 1.97. The reasonable level of agreement can be used to rule out a gross error in the computation of the $3d$ state.

Table 3. The dipole, quadrupole and tensor polarizabilities (for dipole excitations) for the low lying states of Mg^+ and Ca^+. A description of the other calculations can be found in the text [20,79]. The quadrupole moments are computed for $L = M$ which are the same as the $J = M_J = L + 1/2$ state. Numbers in brackets are estimates of the uncertainties in the last digits.

State	α_1 (a.u.)		$\alpha_{1,2LL}$ (a.u.)	α_2 (a.u.)		α_3 (a.u.)	Q_{LL}
	Present	Other	Present	Present	Other	Present	Present
			Mg^+				
$3s$	35.01	34.6 RCC [79] 35.1 $f^{(1)}$-sums [80] 33.8 Experiment [26] 35.02(4) Experiment [81]	0	156.1	156.2 RCC [79]	1715	0
$3p$	31.81	131.2 $f^{(1)}$-sums [20]	1.163	341.7		1.184[4]	−2.756
$4s$	555.1		0	6.751[4]		6.942[5]	0
$3d$	188.6		−112.1	−9.610[3]		2.855[5]	−8.438
$4p$	113.5		77.45	2.713[4]		2.435[6]	−13.41
			Ca^+				
$4s$	75.49	73.89 RCC [79] 76.1(1.1) MBPT [76] 74.05 $f^{(1)}$-sums [80]	0	875.1	706.6 RCC [79]	8990	0
$3d$	32.73	28.7 $f^{(1)}$-sums [20] 32.1(1.1) MBPT [76]	−25.20	−2.844		5.220[3]	−1.819
$4p$	−2.032	3.19 $f^{(1)}$-sums [20]	10.47	1.080[3]		4.126[4]	−4.239
$5s$	983.5			7.281[4]		2.468[6]	0
$4d$	1209		−879.8	1618		3.639[6]	−16.59
$5p$	−1135		286.2	7.123[4]		3.335[6]	−12.67

It is somewhat surprising, but few large scale ab-initio calculations of the oscillator strengths have been performed for any other transitions. Accordingly, comparisons with the model potential (MP) calculations of Melendez et al. [78] for these other transitions in Table 2 are made. The comparisons cannot provide a stringent test of the present calculation, rather they are mainly suitable for detecting gross errors.

3.5 Quadrupole moments

Of the quadrupole moments given in Table 3, the one of most interest is that of the Ca^+ $3d$ state. This is due to the possible use of the Ca^+ $3d \to 4s$ transition as an optical frequency standard [87].

The quadrupole moment of this state has recently been determined in two recent large scale calculations [87,88]. The relativistic configuration interaction (RCI) calculations of Itano et al. [87] gave quadrupole moments of $Q_{3/2} = 1.338$ a.u. and $Q_{5/2} = 1.917$ a.u. for the $3d_{3/2}$ and $3d_{5/2}$ states respectively. The relativistic coupled-cluster (RCC) approach recently gave quadrupole moments of $Q_{3/2} = 1.338$ a.u. and $Q_{5/2} = 1.916$ a.u. [88]. A recent experiment has determined the quadrupole moment, $Q_{5/2}$, to be 1.83(1) a.u. [7].

The present estimate of the quadrupole moment for the $3d$ level is 1.819 a.u., which is some 5% smaller than the two calculations, but close to the recent experiment. The polarization correction to the quadrupole operator makes a substantial contribution to $Q_{5/2}$. Evaluation of the quadrupole expectation value without the polarization correction gives $Q_{5/2} = 1.985$ a.u. Examination of the convergence pattern of the RCI calculation reveals that substantial cancellations exist between some quite large terms. So the apparently very precise agreement between the RCI and RCC calculations could easily be accidental. While the present calculation is not definitive, it does raise questions about the precision of the RCC and RCI estimates of the quadrupole moments.

3.6 Mg^+ polarizabilities

There has been a direct determination of the Mg^+ ground state polarizability from the energy differences of high angular momentum states [26]. The value obtained was $33.8^{+0.5}_{-0.3}$ a_0^3. Polarizabilities of the lowest states of Mg^+ are listed in Table 3 and present calculation gave 35.01 a_0^3 This is closer to the determination of the Theodosiou et al. [80], $\alpha_d = 35.1$ a_0^3 which used the most accurate estimates of the Mg^+ oscillator strengths in the usual sum rule (note, the present core polarizability has been added to the polarizability given in [80]). A more recent experiment by Snow and Lundeen which deduced the Mg^+ polarizabilities from the fine structure of high-ℓ Rydberg levels [81] gave $\alpha_d = 35.02(0.04)$ a_0^3. The recent calculation, and the results of Theodosiou [80] and Snow [81] strongly suggest that the dipole polarizability of Mg^+ is close to 35.0 a_0^3 Snow also reports the coefficient of the $1/r^6$ term of the polarization interactions as $(\alpha_q - 6\beta) = -434 \pm 48$ a_0^3 where β is the non-adiabatic dipole polarizability [81,89]. The present calculation gives a non-adiabatic dipole polarizability of $\beta = 105.83$ a_0^5, yielding $(\alpha_q - 6\beta) = -478.9 \pm 48$ a_0^5 which lies within the error limits of Snow.

The polarizability for the $3p$ state is actually smaller than that of the ground state, most probably due to the contribution from the downward transition to the ground state. This is different from most of the alkali metals which have the dipole polarizability of the np excited state larger than that of the ground state [28].

3.7 Ca$^+$ polarizabilities

The polarizabilities of the lowest six levels of Ca$^+$ are listed in Table 3 and compared with the results of other calculations. The dipole polarizability for the ground state, 75.49 a_0^3 is about 2% larger than an independent estimates that should be reasonably precise. Theodosiou et al. [80] used a single electron Coulomb Approximation which gave a statistically averaged $4p$ lifetime of 6.94×10^{-9} (i.e. the same as an experiment [83]) to estimate a valence polarizability of 74.05 a_0^3 (note, a core polarizability of 3.16 a_0^3 was been added to their valence polarizability of 70.89 a_0^3). Another estimate of 73.89 a_0^3 comes from an all-electron relativistic coupled cluster (RCC) calculation [79]. It is most likely that the current polarizability is too large by 1–2% since the $4p$ lifetime suggests that the resonant oscillator strength is too large by 1–2%.

The ground state quadrupole polarizability of 875.1 a_0^5 is about 20% larger than the RCC polarizability of 706.6 a_0^5 [79]. More than 93% of the polarizability arises from the transitions to the $3d$ and $4d$ states and the transition to the $3d$ level contributes about 65% of the final polarizability. The large discrepancy in the polarizability is especially puzzling since we have computed the quadrupole polarizability of Mg$^+$ using the present approach, and obtain a value that agrees with the RCC α_q of 156.2 a.u. [79] to within 1%. There are some other calculations of the quadrupole polarizability for Ca$^+$ [90,91], but the approximations used in these earlier calculations are sufficiently gross so as to exclude them shedding light on the present discrepancy.

The $f^{(2)}_{4s\rightarrow 3d}$ oscillator strength contributes 523.4 a_0^3 to α_q. The next term involving the $f^{(2)}_{4s\rightarrow 4d}$ oscillator strength contributes 296.9 a_0^3. Changing $f^{(2)}_{4s\rightarrow 3d}$ to the experimental value of 1.90 would reduce its contribution to α_q to 488.5 a_0^3. A large reduction in $f^{(2)}_{4s\rightarrow 4d}$ of order 50% would then be required to get an α_q that agreed with the relativistic coupled cluster (RCC) value of 706.6 a_0^3. Such a change does not seem feasible. First, this oscillator strength was insensitive to changes in the model potential, changing ρ_2 to 1.8316 resulted in a downward shift of the $4d$ level by 0.001 Hartree, while *increasing* the $f^{(2)}_{4s\rightarrow 4d}$ oscillator strength by 2%. Second, the oscillator strength was not very sensitive to modifications in the polarization correction to the transition operator, omitting the correction completely changed $f^{(2)}_{4s\rightarrow 4d}$ by less than 0.1%. The good agreement of $f^{(1)}_{4p\rightarrow 4d}$ with the independent model potential value (see Tab. 2) [78] eliminates the possibility of a gross error in the shape of the $4d$ wave function. The most likely source of error lies in the RCC calculation [79].

The dipole polarizability of the $3d$ level is smaller than that of the $4s$ level because there are no strong transitions originating from this level. The present polarizability is in agreement with the recent MBPT calculation [76] to within the quoted uncertainty.

The difference between the polarizabilities of the $4s$ and $3d$ states contributes to the black-body shift through the approximate result [76],

$$\Delta\nu = -\frac{1}{2}\,(831.9\ \mathrm{V/m})^2 \left(\frac{T(\mathrm{K})}{300}\right)^4 (\alpha_d(3d) - \alpha_d(4s)) \,. \tag{7}$$

The polarizabilities in equation (7) are assumed to be in SI units which can be obtained by multiplying the values in Table 3 by 2.48832×10^{-8} [76]. Using the present polarizabilities gives $\Delta\nu = 0.368$ Hz at 300 K, in reasonable agreement with the recent MBPT value of 0.38 ± 0.01 Hz [76].

The present polarizabilities for the excited states of Ca$^+$ in most cases represent the only calculations of the polarizabilities for these states. One other calculation is based on summing oscillator strengths from tabulations [20] and the overall level of agreement is within ± 5 a_0^3. One curiosity is the very small polarizability of -2.032 a_0^3 for the $4p$ state. This is caused by cancellations between the negative oscillator strengths for downward transitions and the positive oscillator strengths for upward transitions.

4 Long range interactions with buffer atoms

The polarization interaction between the charged ion and any neutral specifies depends on the polarizabilities of the neutral species. A recent tabulation of polarizabilities for the rare gases can be found in a recent paper that reported dispersion interactions of Na and Mg with the rare gases [55]. No more will be said on this topic since our main interest is in those long range interactions that will contribute to a frequency shift between two different ion states, and the polarization interaction does not lead to a frequency shift.

4.1 Mg$^+$ dispersion coefficients with buffer atoms

The dispersion coefficients of a number of Mg$^+$ states interacting with hydrogen and the rare gases are listed in Tables 4, 5 and 6. There is relatively little data available for comparison [17,20]. It is not absolutely clear how the Monteiro et al. [17] estimates were determined so they are not quoted here.

The C_6 estimate of Barklem et al. [20] for the Mg$^+$($3s$)-H configuration uses the Mg$^+$ oscillator strengths which are taken from experiment and the coulomb approximation [80]. As such, there is no contribution from the Mg^{2+} core. However, the hydrogen oscillator

Table 4. The dispersion coefficients (in a.u.) between the $\mathrm{Mg}^+(3s)$, $\mathrm{Mg}^+(4s)$, $\mathrm{Ca}^+(4s)$ and $\mathrm{Ca}^+(5s)$ states and the rare gas atoms and atomic hydrogen. The Barklem et al. estimates [20] used oscillator strength sums to evaluate the dispersion constants. The numbers in the square brackets denote powers of ten.

System	C_6	C_8	C_{10}
	Mg^+		
$\mathrm{Mg}^+(3s)$-H	28.80	7.531[2]	2.511[4]
$f^{(1)}$-sums [20]	27.0		
$\mathrm{Mg}^+(3s)$-He	10.91	2.527[2]	7.461[3]
$\mathrm{Mg}^+(3s)$-Ne	21.58	5.543[2]	1.749[4]
$\mathrm{Mg}^+(3s)$-Ar	80.64	2.437[3]	8.880[4]
$\mathrm{Mg}^+(3s)$-Kr	118.3	3.887[3]	1.544[5]
$\mathrm{Mg}^+(3s)$-Xe	182.9	6.919[4]	3.139[5]
$\mathrm{Mg}^+(4s)$-H	203.6	2.005[4]	2.280[6]
$\mathrm{Mg}^+(4s)$-He	63.90	6.396[3]	7.399[5]
$\mathrm{Mg}^+(4s)$-Ne	123.9	1.273[4]	1.502[6]
$\mathrm{Mg}^+(4s)$-Ar	506.4	5.357[4]	6.418[6]
$\mathrm{Mg}^+(4s)$-Kr	765.0	8.229[4]	9.999[6]
$\mathrm{Mg}^+(4s)$-Xe	1234	1.371[5]	1.712[7]
	Ca^+		
$\mathrm{Ca}^+(4s)$-H	51.78	1.960[3]	8.5372[4]
$f^{(1)}$-sums [20]	43.3		
$\mathrm{Ca}^+(4s)$-He	19.72	659.1	2.692[4]
$\mathrm{Ca}^+(4s)$-Ne	39.14	1.396[3]	5.983[4]
$\mathrm{Ca}^+(4s)$-Ar	145.1	5.967[3]	2.820[5]
$\mathrm{Ca}^+(4s)$-Kr	212.8	9.354[3]	4.696[5]
$\mathrm{Ca}^+(4s)$-Xe	329.1	1.618[4]	8.982[5]
$\mathrm{Ca}^+(5s)$-H	290.0	3.903[4]	5.932[6]
$\mathrm{Ca}^+(5s)$-He	92.23	1.237[4]	1.911[6]
$\mathrm{Ca}^+(5s)$-Ne	179.1	2.443[4]	3.831[6]
$\mathrm{Ca}^+(5s)$-Ar	727.5	1.023[5]	1.621[7]
$\mathrm{Ca}^+(5s)$-Kr	1097	1.566[5]	2.503[7]
$\mathrm{Ca}^+(5s)$-Xe	1764	2.588[5]	4.218[7]

strength distribution is based on an Unsold type approximation [20,92] where the entire distribution is represented by a single term with an appropriately chosen excitation energy. So it is not surprising that the Barklem et al. C_6 estimate of 27.0 a.u. is 5% smaller than the present value of $C_6 = 28.80$ a.u.

The dispersion coefficient for the $\mathrm{Mg}^+(4p)$-H and $\mathrm{Mg}^+(4p)$-He configurations are presented because of the importance of the $4p \rightarrow 3s$ line in astrophysics [23,24].

The accuracy of the dispersion coefficients are estimated at 1–2% for the C_6 values since most of the dipole oscillator strengths relevant to the C_6 calculation have an accuracy approaching this level. The C_8 and C_{10} values involving neon and the heavier rare gases will have larger uncertainties since the quadrupole and octupole pseudo-oscillator strengths are less tightly constrained than the dipole oscillator strengths. A source of error for Mg^+ lies in the small energy difference between the $4s$ and $3d$ levels. The small imperfections in the current energies for these levels will be magnified in the determination of C_8 and C_{10} for the $\mathrm{Mg}^+(4s)$ and $\mathrm{Mg}^+(3d)$.

Table 5. The dispersion coefficients (in a.u.) between the $\mathrm{Mg}^+(3p)$, $\mathrm{Mg}^+(4p)$ and $\mathrm{Ca}^+(4p)$ states and the rare gas atoms and atomic hydrogen. The Barklem et al. estimates [20] used oscillator strength sums to evaluate the dispersion constants. The numbers in the square brackets denote powers of ten.

System		C_6	C_8	C_{10}
		Mg^+		
$\mathrm{Mg}^+(3p)$-H	Σ	85.62	4.969[3]	2.465[5]
$\mathrm{Mg}^+(3p)$-H	Π	41.90	426.7	1.066[4]
$f^{(1)}$-sums [20]	Σ	110.5		
$f^{(1)}$-sums [20]	Π	63.1		
$\mathrm{Mg}^+(3p)$-He	Σ	25.79	1.670[3]	7.984[4]
$\mathrm{Mg}^+(3p)$-He	Π	14.23	95.56	1.815[3]
$\mathrm{Mg}^+(3p)$-Ne	Σ	50.26	3.387[3]	1.722[5]
$\mathrm{Mg}^+(3p)$-Ne	Π	27.97	266.8	5.543[3]
$\mathrm{Mg}^+(3p)$-Ar	Σ	205.5	1.408[4]	7.766[5]
$\mathrm{Mg}^+(3p)$-Ar	Π	108.9	1.561[3]	4.344[4]
$\mathrm{Mg}^+(3p)$-Kr	Σ	313.1	2.167[4]	1.261[6]
$\mathrm{Mg}^+(3p)$-Kr	Π	162.6	2.790[3]	9.031[4]
$\mathrm{Mg}^+(3p)$-Xe	Σ	514.3	3.646[4]	2.312[6]
$\mathrm{Mg}^+(3p)$-Xe	Π	258.4	5.813[3]	2.240[5]
$\mathrm{Mg}^+(4p)$-H	Σ	415.5	1.160[5]	1.943[7]
$\mathrm{Mg}^+(4p)$-H	Π	230.9	4.335[3]	3.049[5]
$\mathrm{Mg}^+(4p)$-He	Σ	128.8	3.676[4]	6.232[6]
$\mathrm{Mg}^+(4p)$-He	Π	73.06	1.268[3]	9.754[4]
		Ca^+		
$\mathrm{Ca}^+(4p)$-H	Σ	132.0	1.193[4]	7.954[5]
$\mathrm{Ca}^+(4p)$-H	Π	72.31	818.0	2.461[4]
$f^{(1)}$-sums [20]	Σ	114.5		
$f^{(1)}$-sums [20]	Π	65.4		
$\mathrm{Ca}^+(4p)$-He	Σ	42.11	3.948[3]	2.599[5]
$\mathrm{Ca}^+(4p)$-He	Π	25.04	225.7	5.215[3]
$\mathrm{Ca}^+(4p)$-Ne	Σ	82.28	7.896[3]	5.442[5]
$\mathrm{Ca}^+(4p)$-Ne	Π	49.36	584.6	1.464[4]
$\mathrm{Ca}^+(4p)$-Ar	Σ	329.7	3.261[4]	2.379[6]
$\mathrm{Ca}^+(4p)$-Ar	Π	190.2	3.080[3]	9.827[4]
$\mathrm{Ca}^+(4p)$-Kr	Σ	497.4	4.983[4]	3.774[6]
$\mathrm{Ca}^+(4p)$-Kr	Π	283.2	5.324[3]	1.935[5]
$\mathrm{Ca}^+(4p)$-Xe	Σ	802.6	8.250[4]	6.672[6]
$\mathrm{Ca}^+(4p)$-Xe	Π	448.5	1.065[4]	4.547[5]

4.2 Ca^+ dispersion coefficients with buffer atoms

The dispersion coefficients for the Ca^+ ground state interacting with hydrogen and the rare gases are listed in Table 4. Dispersion coefficients involving the $4p$ and $3d$ excited states are given in Tables 5 and 6 respectively.

The Ca^+(4s)-H value of C_6 is about 20% larger than the value of Barklem et al. [20] for reasons discussed in the previous section. There are no other estimates of dispersion coefficients involving the Ca^+ ground state with any other atom.

The dispersion coefficients for the $3d$ states are about twice as large as the values of Barklem et al. [20]. This is probably due to the omission of the $3d \rightarrow \epsilon\ell$ continuum in the intermediate sum of Barklem et al. The total oscillator strength sum of Barklem et al. for dipole transitions originating from the $3d$ level, i.e. $\sum_i f^{(1)}_{3d\rightarrow nl}$ was

Table 6. The dispersion coefficients (in a.u.) between the $3d$ states of Mg^+ and Ca^+ and the rare gas atoms and atomic hydrogen. The Barklem et al. estimates [20] used oscillator strength sums to evaluate the dispersion constants. The numbers in the square brackets denote powers of ten.

System		C_6	C_8	C_{10}
		Mg^+		
$\mathrm{Mg}^+(3d)$-H	Σ	170.5	3.044[4]	3.753[6]
$\mathrm{Mg}^+(3d)$-H	Π	149.7	1.015[4]	2.710[5]
$\mathrm{Mg}^+(3d)$-H	Δ	87.30	−866.5	−4.094[3]
$\mathrm{Mg}^+(3d)$-He	Σ	51.64	8.922[3]	1.213[6]
$\mathrm{Mg}^+(3d)$-He	Π	45.76	3.157[3]	7.551[4]
$\mathrm{Mg}^+(3d)$-He	Δ	28.13	−382.2	−2.458[3]
$\mathrm{Mg}^+(3d)$-Ne	Σ	100.2	1.755[4]	2.432[6]
$\mathrm{Mg}^+(3d)$-Ne	Π	88.84	6.378[3]	1.843[5]
$\mathrm{Mg}^+(3d)$-Ne	Δ	54.82	−580.5	−4.967[3]
$\mathrm{Mg}^+(3d)$-Ar	Σ	412.7	7.383[4]	1.025[7]
$\mathrm{Mg}^+(3d)$-Ar	Π	364.6	2.693[4]	9.652[5]
$\mathrm{Mg}^+(3d)$-Ar	Δ	220.1	−1.265[3]	−3.173[3]
$\mathrm{Mg}^+(3d)$-Kr	Σ	627.5	1.142[5]	1.583[7]
$\mathrm{Mg}^+(3d)$-Kr	Π	553.5	4.194[4]	1.686[6]
$\mathrm{Mg}^+(3d)$-Kr	Δ	331.2	−942.94	2.408[4]
$\mathrm{Mg}^+(3d)$-Xe	Σ	1025	1.830[5]	2.677[7]
$\mathrm{Mg}^+(3d)$-Xe	Π	902.1	6.857[4]	3.467[6]
$\mathrm{Mg}^+(3d)$-Xe	Δ	532.6	1.388[3]	1.356[5]
		Ca^+		
$\mathrm{Ca}^+(3d)$-H	Σ	27.16	1.910[3]	1.088[5]
$\mathrm{Ca}^+(3d)$-H	Π	24.75	752.6	1.550[4]
$\mathrm{Ca}^+(3d)$-H	Δ	17.51	152.6	3.191[3]
$f^{(1)}$-sums [20]	Σ	15.7		
$f^{(1)}$-sums [20]	Π	13.9		
$f^{(1)}$-sums [20]	Δ	8.7		
$\mathrm{Ca}^+(3d)$-He	Σ	11.36	644.8	3.576[4]
$\mathrm{Ca}^+(3d)$-He	Π	10.52	260.7	3.387[3]
$\mathrm{Ca}^+(3d)$-He	Δ	8.008	36.20	385.1
$\mathrm{Ca}^+(3d)$-Ne	Σ	22.95	1.323[3]	7.584[4]
$\mathrm{Ca}^+(3d)$-Ne	Π	21.31	572.1	9.771[3]
$\mathrm{Ca}^+(3d)$-Ne	Δ	16.40	118.9	1.515[3]
$\mathrm{Ca}^+(3d)$-Ar	Σ	80.34	5.441[3]	3.334[5]
$\mathrm{Ca}^+(3d)$-Ar	Π	73.93	2.425[3]	6.163[4]
$\mathrm{Ca}^+(3d)$-Ar	Δ	54.71	669.3	1.464[4]
$\mathrm{Ca}^+(3d)$-Kr	Σ	116.3	8.352[3]	5.326[5]
$\mathrm{Ca}^+(3d)$-Kr	Π	106.8	3.823[3]	1.152[5]
$\mathrm{Ca}^+(3d)$-Kr	Δ	78.24	1.192[3]	3.125[4]
$\mathrm{Ca}^+(3d)$-Xe	Σ	177.0	1.393[4]	9.541[5]
$\mathrm{Ca}^+(3d)$-Xe	Π	162.0	6.673[3]	2.543[5]
$\mathrm{Ca}^+(3d)$-Xe	Δ	117.1	2.435[3]	8.013[4]

only 0.444 whereas a number closer to unity would have been expected. The omission of the core by Barklem et al. can also be expected to result in the dispersion coefficients being underestimated.

The dispersion coefficients of the $3d$ level are generally smaller than the dispersion coefficients of the $4s$ level. This occurs because there are no strong transitions between the $3d$ level and the other low lying levels of Ca^+ (refer to dipole oscillator strengths in Tab. 2). The lack of any strong transitions to the low lying states also manifested itself in the smaller polarizabilities of the $3d$ state.

Given that the polarizability of the $4p$ state is so small it is surprising that the dispersion coefficients involving this state are larger than those involving the $4s$ ground state. This is explained by the energy distribution of the $4p$ oscillator strength set. The transitions to the $3d$ and $4s$ states with negative oscillator strengths involve smaller transition energies than any of the upward transitions. So the impact of the downward transitions is maximized in the polarizability calculation with its $1/\Delta E^2$ energy denominator, but the downward transitions have less impact in the C_6 calculation which involves different energy weighting factors.

The overall accuracy of the dispersion coefficients involving the $\mathrm{Ca}^+(4s)$ and $\mathrm{Ca}^+(4p)$ states should be comparable to those involving the $3s$ and $3p$ states of Mg^+. In cases where transition moments involving the $3d$ state make a significant contribution one can expect the uncertainties in the derived C_n coefficients to be larger.

5 Conclusions

A survey of atomic parameters of the Mg^+ and Ca^+ ion states relevant to the description of long range interactions have been computed with a semi-empirical method. The most important parameters are the dispersion coefficients of the excited states with the buffer gases as there is little quantitative data (e.g. Ref. [20]) despite the large number of pressure broadening experiments.

The polarizabilities and dispersion coefficients for the $\mathrm{Ca}^+(4s)$ and $\mathrm{Ca}^+(3d)$ states are relevant to the utilization of the $3d \rightarrow 4s$ transition as an optical frequency standard [3,4,6,87]. The difference between the two polarizabilities contributes to the black-body shift in the transition frequency. The differences between the dispersion constants can be used to give an initial estimate of the pressure shift of the Ca^+ $4s$-$3d$ transition in a rare gas buffer by using the impact approximation [21,22]. It would be straightforward to compute the polarizabilities and dispersion coefficients of other alkaline-earth ions.

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