Long-range interactions between alkali and alkaline-earth atoms

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Abstract
Dispersion coefficients between the alkali metal atoms (Li–Rb) and alkaline-earth metal atoms (Be–Sr) are evaluated using matrix elements computed from frozen core configuration interaction calculations. Besides dispersion coefficients with both atoms in their respective ground states, dispersion coefficients are also given for the case where one atom is in its ground state and the other is in a low-lying excited state.

1. Introduction

Recently a systematic ab initio investigation of the ground state potential curves for the MgX dimers, where X is an alkali atom, was reported [1]. The motivation for this work was the growing interest in the production of molecules from ultracold atomic gases [2]. Such molecules can be formed by photo-association [3, 4], or by Feshbach resonance tuning [5, 6]. Most focus has been on diatomic molecules consisting of two alkali atoms [7–10]. However it has been suggested that ultracold molecules in \( ^2\Sigma \) states would be good systems for experiments on controlled chemical reactions [11]. Such molecules could be formed from an alkali atom in its ground state and an alkaline-earth atom (or Yb) in its ground state. Recently, the vibrational spectra of CaLi and SrLi were investigated for their sensitivity to the \( m_r/M_r \) mass ratio [12]. There have been previous studies of the structure of alkali/alkaline-earth dimers [13–18]. The most recent theoretical investigations of these molecules motivated by cold atom physics include LiSr [19], LiYb [20, 21], RbSr [22] and RbYb [23–25]. A more comprehensive investigation has been made of the LiX dimers, where X is a alkaline-earth atom [26, 27].

The present paper investigates the long-range interaction of various combinations of alkali and alkaline-earth atoms. The most efficient method for determining the long-range interaction is by computing the dispersion coefficients since this leads to the factorization of one large many-body calculation into two smaller many-body calculations. The dispersion coefficient calculations were not restricted to the respective ground states. Dispersion coefficients are also given for an alkali atom in its ground state and the nsnp \(^3\Pi\)o and nsnp \(^1\Pi\)o excited states of the alkaline-earth atoms. Coefficients are given for the nsnd \(^1\Sigma\)o excited states of calcium and strontium since these nsnd \(^1\Delta\)o states have a smaller excitation energy than the nsnp \(^1\Pi\)o excited states. The dispersion coefficients for the alkaline-earth atoms in their ground states and three of the lowest excited states of the alkali atoms are also given. The present work gives a comprehensive overview of the long-range interactions between the ground and the low-lying excited states of the alkali/alkaline-earth dimers.

2. Methodology of calculation

2.1. Overview of van der Waals interaction calculation

The long-range van der Waals interaction between two heteronuclear atoms (i.e. the two atoms are different), with one atom in an S-state, can be as a function of inter-nuclear separation, \( R \), written [28–30]

\[
V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots
\]

The \( C_n \) parameters are the dispersion coefficients.

The approach used to generate the dispersion coefficients is based on the use of oscillator strength sum rules [28, 29]. This reduces 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. In practice, a pseudo-state representation is used which gives a discrete representation of the continuum [30–32]. 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 \( L > 0 \) [30].

The major part of any calculation involves the generation of the lists of reduced transition matrix elements.
The static dipole ($\alpha_1$) and quadrupole ($\alpha_2$) polarizabilities (in au) for the ground states of the alkali and alkaline-earth atoms. A recent review summarizes static dipole polarizabilities calculations and experiments [42].

| Atom | CICP | MBPT-SD | Other |
|------|------|---------|-------|
| $\alpha_1$ Li | 164.21 | 164.08 | 164.11(3) (Hylleraas) [44] |
| $\alpha_1$ Na | 162.8 | 163.0 | 164.2(1.1) Experiment [45] |
| $\alpha_1$ K | 290.0 | 289.1 | 162.6(3) (Hybrid) [46] |
| $\alpha_1$ Rb | 315.7 | 317.4 | 162.7(8) Experiment [47] |
| $\alpha_1$ Li | 1424 | 1424(4) [49] |
| $\alpha_1$ Na | 1879 | 1885(26) [49] |
| $\alpha_1$ K | 5005 | 5000(45) [49] |
| $\alpha_1$ Rb | 6480 | 6520(80) [49] |

Table 2. The dispersion coefficients (in au) for the ground state of alkalai atoms interacting with the ground states of alkaline-earth atoms. The numbers in the square brackets denote powers of ten. $C_n$ coefficients derived from MBPT-SD and Cl+MBPT dynamic polarizability [64] are given in the rows with no other $C_n$ coefficients and have estimated errors given by the numbers in brackets. The notation $a[b]$ means $a \times 10^b$.

| $C_8$ | $C_9$ | $C_{10}$ |
|-------|-------|---------|
| Be(2$^2$ 1S$^o$) | 1.743[4] | 1.038[6] |
| Na(3s) | 2.196[4] | 1.403[6] |
| K(4s) | 4.775[4] | 3.924[6] |
| Rb(5s) | 5.818[4] | 5.076[6] |
| Mg(3$^2$ 1S$^o$) | 5.676[4] | 4.535[6] |
| Na(3s) | 6.727[4] | 5.735[6] |
| K(4s) | 1.282[5] | 1.333[7] |
| Rb(5s) | 1.513[5] | 1.660[7] |
| Ca(4s$^2$ 1S$^o$) | 1.417[5] | 1.263[7] |
| Na(3s) | 1.637[5] | 1.564[7] |
| K(4s) | 3.030[5] | 3.468[7] |
| Rb(5s) | 3.535[5] | 4.268[7] |
| Sr(5$^x$ 1S$^o$) | 1.898[5] | 1.789[7] |
| Na(3s) | 2.172[5] | 2.194[7] |
| K(4s) | 3.971[5] | 4.765[7] |
| Rb(5s) | 4.609[5] | 5.833[7] |

for the two atomic states. This involves quite lengthy calculations to generate the excitation spectrum of the pseudo-state representation. It is then a relatively straightforward calculation to process the lists of matrix elements and generate the dispersion coefficients [30, 33].

2.2. Structure model: the alkali atoms

The transition arrays for the alkali atoms are essentially those which were used in calculations of the dispersion interactions between these atoms and the ground states of hydrogen and helium [30].

These were computed by diagonalizing the fixed core Hamiltonian in a large basis of Laguerre type orbitals (LTO). The core Hamiltonian is based upon a Hartree–Fock (HF) description of the core with a semi-empirical core polarization potential tuned to reproduce the energies of the low-lying spectrum. The oscillator strengths (and other multipole expectation values) were computed with operators that included polarization corrections [32, 34–37].

Core excitations are included in the $C_n$ calculations. Oscillator strength distributions were constructed by using independent estimates of the core polarizabilities to constrain the sum rules [32, 38, 39, 40]. The methodology of using constrained sum rules to construct pseudo-oscillator strength distributions has been widely used [41].

2.3. The alkaline-earth atoms

The use of a fixed core model reduces the calculation of the alkaline-earths and their excited spectra to a two electron calculation. The two electron wavefunctions were expanded in a large basis of two electron configurations formed from a single electron basis mostly consisting of LTO. Typically the total number of one electron states would range from 150 to 200. The use of such large basis sets means that the error due to incompleteness of the basis is typically very small. The semi-empirical polarization potential needs to include a two-body term to deal with the instantaneous interaction between the core and the two valence electrons that may be on opposite sides of the nucleus [32, 35, 57].

Details of the calculations used to represent Be, Mg, Ca and Sr have been previously described [33, 58–61]. We refer to these semi-empirical models of atomic structure as the configuration interaction plus core polarization (CICP) model in subsequent text. The matrix element set for Sr incorporated experimental information. An experimental value was used for the 5s$^2$ 1S$^o$–5s5p 1P$^o$ matrix element [62] and the
Table 3. The dispersion coefficients (in au) for the ground state of alkali atoms interacting with the \( nsp^1P^o \) and \( 3P^o \) excited states of alkaline-earth atoms. \( n = 2, 3, 4 \) and 5 for Be, Mg, Ca and Sr, respectively. The notation \( a[b] \) means \( a \times 10^b \). Dispersion coefficients which could be influenced by an accidental degeneracy with pseudo-states in the alkali atom continuum are indicated by underlining.

| \( nsp^1P^o \) | \( C_6 \) | \( C_8 \) | \( C_{10} \) | \( nsp^3P^o \) | \( C_6 \) | \( C_8 \) | \( C_{10} \) |
|----------------|-------|-------|-------|----------------|-------|-------|-------|
| **Be**         |       |       |       | **Be**         |       |       |       |
| Li(2s)         | 1.228 | 3.270 | 4.737 | 8.122         | 1.751 | 1.043 |       |
| \( \Sigma \)   | 9.516 | 2.725 | 1.882 | 4.930         | 1.785 | 1.061 |       |
| Na(3s)         | 1.176 | 3.650 | 1.530 | 5.248         | 2.206 | 1.410 |       |
| \( \Sigma \)   | 9.883 | 2.335 | 6.321 | 5.377         | 2.250 | 1.435 |       |
| K(4s)          | 2.173 | 7.630 | -5.181| 7.970         | 4.807 | 3.948 |       |
| \( \Pi \)      | 1.611 | 8.056 | 2.163 | 8.161         | 4.902 | 4.017 |       |
| Rb(5s)         | 2.444 | 9.739 | 3.600 | 8.756         | 5.861 | 5.109 |       |
| \( \Sigma \)   | 1.778 | 1.002 | 7.443 | 8.964         | 5.976 | 5.199 |       |

| **Mg**         |       |       |       | **Mg**         |       |       |       |
| Li(2s)         | 2.310 | 7.052 | 1.340 | 1.244         | 2.598 | 2.431 |       |
| \( \Sigma \)   | 1.835 | 7.147 | 1.472 | 1.063         | 5.923 | 3.840 |       |
| Na(3s)         | 2.239 | 4.099 | 8.929 | 1.337         | 2.814 | 2.925 |       |
| \( \Sigma \)   | 1.396 | -2.585 | -5.971| 1.148         | 6.921 | 5.053 |       |
| K(4s)          | 4.148 | 1.300 | 1.967 | 2.060         | 4.879 | 6.091 |       |
| \( \Pi \)      | 3.131 | 2.038 | 4.813 | 1.760         | 1.443 | 1.330 |       |
| Rb(5s)         | 4.629 | 1.537 | 2.606 | 2.252         | 5.489 | 7.382 |       |
| \( \Sigma \)   | 3.442 | 2.783 | 1.870 | 1.926         | 1.719 | 1.708 |       |

| **Ca**         |       |       |       | **Ca**         |       |       |       |
| Li(2s)         | -5.557| 1.082 | 1.515 | 2.307         | 6.241 | 6.699 |       |
| \( \Sigma \)   | 1.474 | 2.310 | 1.714 | 2.065         | 1.205 | 8.890 |       |
| Na(3s)         | -2.476| 1.281 | 1.742 | 2.438         | 6.652 | 7.864 |       |
| \( \Sigma \)   | 1.096 | 3.046 | 2.209 | 2.188         | 1.405 | 1.145 |       |
| K(4s)          | 1.164 | -9.103 | 3.670 | 3.871         | 1.151 | 1.590 |       |
| \( \Pi \)      | 2.983 | -1.946 | 6.467 | 3.461         | 2.866 | 2.884 |       |
| Rb(5s)         | 4.641 | 8.794 | 4.611 | 4.223         | 1.287 | 1.908 |       |
| \( \Sigma \)   | 4.099 | 1.348 | 9.109 | 3.778         | 3.442 | 3.664 |       |

| **Sr**         |       |       |       | **Sr**         |       |       |       |
| Li(2s)         | -1.753| 1.408 | 2.240 | 3.116         | 9.286 | 1.086 |       |
| \( \Sigma \)   | 1.560 | 2.695 | 2.235 | 2.718         | 1.575 | 1.257 |       |
| Na(3s)         | -5.563| 1.589 | 2.541 | 3.270         | 9.838 | 1.266 |       |
| \( \Sigma \)   | 7.231 | 3.403 | 2.831 | 2.860         | 1.842 | 1.602 |       |
| K(4s)          | 3.002 | -2.382 | 5.054 | 5.257         | 1.703 | 2.517 |       |
| \( \Pi \)      | 3.428 | -8.213 | 7.551 | 4.582         | 3.769 | 3.962 |       |
| Rb(5s)         | 1.068 | 4.886 | 6.078 | 5.735         | 1.899 | 3.082 |       |
| \( \Sigma \)   | 3.927 | -1.103 | 9.973 | 5.000         | 4.503 | 5.009 |       |

The agreement with experiment or hybrid experimental/theoretical estimates of the static dipole polarizability for Li, Na and K is better than 0.5%. The level of agreement is 1% for rubidium where relativistic effects are more important. There is close agreement between CICP and MBPT-SD [49] quadrupole polarizabilities for the alkali atoms.
calcium and strontium. The notation achieved with the experimental value [69].

Agreement was a relativistic variant of the present calculation [71] was used to tune-out wavelengths for potassium. Additional information such as magic wavelengths and tune-out wavelengths also give information on the excited state polarizabilities using the CICP method have been given [30, 33, 40, 58–61]. The polarizabilities of potassium serve as an indicative example. CICP calculations gave 615 au for K(4p), 4997 au for K(5s), and 1419 au for K(3d) [30]. MBPT-SD calculations give 611 au for K(4p3/2), 620 au for K(4p1/2), 4961 au for K(5s1/2), 1420 au for K(3d3/2), and 1412 au for K(3d5/2) [73]. The evaluation of the oscillator strength sum rules in previous CICP investigations often used calculated energy differences. While this has only a small effect on the ground state polarizabilities, the use of calculated energy differences will introduce larger differences when applied to excited states where the energy differences are smaller and thereby making the polarizabilities more sensitive to small errors in the calculated energies. Spin–orbit energy splittings can also impact polarizabilities of the excited states for the heavier atoms. For example, the static dipole polarizabilities of the 5p spin–orbit doublet differ by 8% [74] and the present dispersion coefficients should be interpreted as the average for a spin–orbit doublet or triplet state.

### 3.2. Ground state dispersion coefficients

Table 2 lists the $C_6$, $C_8$ and $C_{10}$ dispersion coefficients between all combinations consisting of a ground state alkali atom and a ground state alkaline-earth atom. There have been two previous comprehensive tabulations of $C_6$ coefficients for these combinations of atoms. The tabulation by Standard and Certain [75] can be regarded as obsolete [32]. More recently, dynamic polarizabilities from MBPT-SD and CI+MBPT calculations have been used to estimate dispersion coefficients for many alkali/alkaline-earth dimers [64]. However these calculations were restricted to the lowest order $C_6$ coefficients.
resonance transition. This values which use an experimental matrix element for the than the hybrid CI+MBPT calculation of $1\alpha_1$. The largest differences occur for the dimers involving calcium, where the CICP values of $6\alpha_1$ for calcium were just over 1% larger than 1%. There is also better than 1% agreement between the CICP values of $1\alpha_1$ for calcium were just over 1% larger than the CI+MBPT calculation of $1\alpha_1$. The presence of a downward transition for the $1\alpha_1$ excited state makes it possible for the dispersion coefficients to be negative, thereby indicating a repulsive dispersion interaction. Contributions of the $C_6$ coefficients can be negative when the total energy of the transitions originating from the two atoms is negative. The $1\alpha_1$ state does not have a spin-allowed transition to the ground state so all the dispersion coefficients are positive. Examples of a negative $C_6$ coefficient occur for some of the $\Sigma$ states in table 3.

Table 3 exhibits some expected trends. The $C_6$ coefficients tend to increase as the alkali atoms get larger in the Li → Rb sequence. This is expected since the polarizabilities increase from Li → Rb. There is also an increase in $C_6$ for the nsnp $1\alpha_1$ states as the atoms increase in size from Be → Sr. This is again a polarizability related increase. A steady increase in nsnp $1\alpha_1$ state $C_6$ values does not occur as the atomic size increases from Mg → Sr. These states have downward transitions and the Mg 3s3p $1\alpha_1$ polarizability [33] is about twice the size of the Sr 5s5p $1\alpha_1$ polarizability [61].

3.3. Dispersion coefficients for the alkaline-earth excited states

Table 3 details the dispersion coefficients for the nsnp $1\alpha_1$ alkaline-earth excited states. In the case of calcium and strontium, the first singlet excited state is actually the $n\Sigma(n−1)d 1\alpha_1$ state. For purposes of completeness, dispersion coefficients between the $n\Sigma(n−1)d 1\alpha_1$ states of calcium and strontium with the alkali ground states are listed in table 4.

The presence of a downward transition for the $1\alpha_1$ excited state makes it possible for the dispersion coefficients to be negative, thereby indicating a repulsive dispersion interaction. Contributions of the $C_6$ coefficients can be negative when the total energy of the transitions originating from the two atoms is negative. The $1\alpha_1$ state does not have a spin-allowed transition to the ground state so all the dispersion coefficients are positive. Examples of a negative $C_6$ coefficient occur for some of the $\Sigma$ states in table 3.

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There are a number of apparent irregularities when examining the $C_n$ values for a sequence of atoms, e.g. from Li $\rightarrow$ K, or Be $\rightarrow$ Sr in table 3 and the later tables. This occurs because the energy denominators in the sum rules for the dispersion coefficients now have single atom excitation energies that can be both positive and negative. For example, negative $C_6$ values occur for some $nsnp \ ^1P^o$ states. What has occurred is that the energy of the downward transition of the alkaline-earth exceeds the energy increase of some of the upward transitions of the alkali atoms. In addition, the energies of the downward transition and the upward transition of the alkali atoms. The numbers in the square brackets denote powers of 10.

There is one potential problem with some of the dispersion coefficients involving excited states when the de-excitation energies from the alkaline-earth excited states are larger than the ionization energies of the alkali atoms. Formally, the energy denominator in the perturbation theory sum rules for these combinations would have a zero arising when the excitation energy in the alkali atom continuum is equal to the de-excitation energy of the $nsnp \ ^1P^o$ excited states. The dispersion interaction in this case will have an imaginary part. There is also the possibility that an accidental near zero energy between the $nsnp \ ^1P^o$ de-excitation energy and the energy of the one of the pseudo-states in the alkali atom pseudo-continuum could lead to an error in the calculation of the dispersion coefficients. The only tabulated $C_n$ coefficients susceptible to this problem occur in table 3. The dimers involved contain either the K and Rb atoms interacting with the Be($2s2p \ ^1P^o)$ and Mg($3s3p \ ^1P^o$) states and the dispersion coefficients that may be susceptible to this problem are underlined in table 3.

While the $nsnp \ ^1P^o$ state is the lowest excited state for Be and Mg, it is not the lowest energy excited state for Ca and Sr. In these cases, the $4s3d \ ^1D^o$ and $5s4d \ ^1D^o$ states are the lowest energy excited states for Ca and Sr respectively. Dispersion coefficients for the $^1D^o$ and $^3D^o$ states are listed in table 4. The $C_6$ coefficients for the $^1D^o$ states are all positive since these states do not have an energy decreasing dipole transition. Some of the $C_10$ coefficients are also negative, this occurs because the transition energies of the $ns \rightarrow (n-1)d$ states are almost the same as transition energies of the $ns(n-1)d \rightarrow ns^2$ transition energies. This leads to the energy denominator in the sum rule used to compute $C_{10}$ [30] being close to zero. The negative $C_6$

| Table 6. The dispersion coefficients (in au) for the lowest $nd$ states of alkali atoms interacting with the ground states of the alkaline-earth atoms. The numbers in the square brackets denote powers of 10. |
|---|---|---|---|---|---|
| | $C_6$ | $C_8$ | $C_{10}$ | $C_8$ | $C_{10}$ |
| **Be($2s^2 \ ^1S^o$)** | | | | | |
| $\Sigma$ | 5.972[3] | 4.208[6] | 2.273[9] | 5.849[3] | 4.073[6] |
| $\Pi$ | 5.274[3] | 1.408[6] | 8.463[7] | 5.167[3] | 1.362[6] |
| $\Delta$ | 3.181[3] | −2.547[5] | −2.674[6] | 3.120[3] | −2.462[5] |
| Mg($3s^2 \ ^1S^o$) | | | | | |
| $\Sigma$ | 1.137[4] | 8.323[6] | 4.581[9] | 1.110[4] | 8.015[6] |
| $\Pi$ | 1.002[4] | 2.905[6] | 3.147[8] | 9.788[3] | 2.801[6] |
| $\Delta$ | 5.984[3] | −2.947[5] | −1.204[7] | 5.857[3] | −2.815[5] |
| Ca($4s^2 \ ^1S^o$) | | | | | |
| $\Sigma$ | 2.711[4] | 1.837[7] | 1.033[10] | 2.564[4] | 1.747[7] |
| $\Pi$ | 2.374[4] | 6.338[6] | 8.662[8] | 2.250[4] | 6.076[6] |
| $\Delta$ | 1.365[4] | −3.631[5] | −3.683[7] | 1.307[4] | −3.435[5] |
| Sr($5s^2 \ ^1S^o$) | | | | | |
| $\Sigma$ | 3.674[4] | 2.416[7] | 1.343[10] | 3.361[4] | 2.283[7] |
| $\Pi$ | 3.206[4] | 8.288[6] | 1.221[9] | 2.943[4] | 7.943[6] |
| $\Delta$ | 1.805[4] | −2.914[5] | −5.324[7] | 1.690[4] | −2.835[5] |

| **K(3d)** | | | | | |
| **Be($2s^2 \ ^1S^o$)** | | | | | |
| $\Sigma$ | 4.147[3] | 2.340[6] | 1.039[9] | 3.327[3] | 1.646[6] |
| $\Pi$ | 3.664[3] | 7.704[5] | 3.625[7] | 2.943[3] | 5.373[5] |
| $\Delta$ | 2.215[3] | −1.396[5] | −1.272[6] | 1.791[3] | −9.586[4] |
| Mg($3s^2 \ ^1S^o$) | | | | | |
| $\Sigma$ | 7.833[3] | 4.626[3] | 2.125[9] | 6.250[3] | 3.271[6] |
| $\Pi$ | 6.907[3] | 1.613[5] | 1.562[8] | 5.516[3] | 1.143[6] |
| $\Delta$ | 4.120[3] | −1.318[5] | −5.260[6] | 3.315[3] | −7.370[4] |
| Ca($4s^2 \ ^1S^o$) | | | | | |
| $\Sigma$ | 1.778[4] | 1.179[7] | 5.300[9] | 1.397[4] | 7.951[6] |
| $\Pi$ | 1.560[4] | 4.092[6] | 6.629[8] | 1.227[4] | 2.782[6] |
| $\Delta$ | 9.046[3] | −9.458[4] | −1.197[5] | 7.150[3] | −6.966[3] |
| Sr($5s^2 \ ^1S^o$) | | | | | |
| $\Sigma$ | 2.226[4] | 3.871[7] | 5.877[9] | 1.740[4] | 1.081[7] |
| $\Pi$ | 1.950[4] | 1.317[7] | 5.303[8] | 1.526[4] | 8.226[2] |
| $\Delta$ | 1.121[4] | 1.211[4] | −2.326[7] | 8.825[3] | 9.168[4] |

| **Rb(4d)** | | | | | |
| **Be($2s^2 \ ^1S^o$)** | | | | | |
| $\Sigma$ | 4.147[3] | 2.340[6] | 1.039[9] | 3.327[3] | 1.646[6] |
| $\Pi$ | 3.664[3] | 7.704[5] | 3.625[7] | 2.943[3] | 5.373[5] |
| $\Delta$ | 2.215[3] | −1.396[5] | −1.272[6] | 1.791[3] | −9.586[4] |
| Mg($3s^2 \ ^1S^o$) | | | | | |
| $\Sigma$ | 7.833[3] | 4.626[3] | 2.125[9] | 6.250[3] | 3.271[6] |
| $\Pi$ | 6.907[3] | 1.613[5] | 1.562[8] | 5.516[3] | 1.143[6] |
| $\Delta$ | 4.120[3] | −1.318[5] | −5.260[6] | 3.315[3] | −7.370[4] |
coefficient for the Na–Sr dimer arises from the near-equality of the 3s → 3p and 5s4d 1D− → 5s2 1S0 transition energies.

All the dispersion coefficients involving the alkaline-earth ns(n − 1)d 3D+ states are positive. This state has an energy decreasing dipole transition to the nsnp 3P+ state. However, the transition energy for this transition is very small and there are no accidental near-equalities in energies with any transitions emanating from the alkali ground states.

3.4. Dispersion coefficients for the alkali excited states

Table 5 gives the dispersion coefficients for the np and (n + 1)s alkali states interacting with the ground states of the alkaline earth atoms. Table 6 gives the dispersion coefficients between the alkaline-earth ground states and the lowest alkaline nd states. All the coefficients are positive.

All the Cn coefficients in table 5 are positive and obey predictable trends. The coefficients get bigger as the alkaline-earth atoms change from beryllium to strontium. The coefficients also increase as the alkali atoms increase in size from lithium to rubidium.

The Cn coefficients in table 6 also obey regular trends. One trend is for the Cn coefficients to decrease as the alkali atoms increase in size from lithium to rubidium. This might seem counterintuitive but the polarizabilities of the lowest alkaline nd states tend to decrease in size from sodium to rubidium [30]. There is also a trend for the Cn values to increase in size for the larger alkaline-earth atoms.

The C6 and C10 coefficients are negative for the dimers with Δ symmetry. This is not the consequence of transitions that decrease energy. Rather, the equations [76, 30] for Cn coefficients of Δ symmetry allow the possibility that the dispersion coefficients can be negative.

4. Conclusions

Large scale CI calculations have been used to generate polarizabilities and dispersion coefficients for many combinations of the alkali and alkaline-earth atoms. The underlying accuracy of the calculation is known by reference to previous calculations using the same structure model [32, 33, 58–61].

The most important coefficients are those for the alkali and alkaline-earth atoms in their respective ground states. These coefficients should be accurate to close to 1% for many combinations and a reasonable upper limit of the maximum error would be 2–3%. Somewhat surprisingly, the only previous tabulation of the full C6, C8 and C10 set for these dimers was the Standard and Certain compilation [75] and the present Cn values in many cases are an order of magnitude more precise (an assessment of the accuracy of Standard and Certain compilation for dimers involving alkaline-earth atoms has already been published [32]). The same degree of precision is not present for dispersion coefficients in dimers containing excited states. The excited state calculations involve de-exiting transitions that can lead to cancellations in the sum rules used for the computation of the Cn coefficients. In these cases, the uncertainties in the dispersion coefficients can easily exceed 10%. These cases can be identified by looking for anomalies in pattern of Cn coefficients during an examination over a group of similar atoms.

One limitation of the present calculation is the absence of the spin–orbit interaction and the use of LS coupling. As mentioned earlier, the difference in the polarizabilities of the Rh(5p) spin–orbit doublet is 8%. This would then translate into similar differences in the Cn coefficients involving this state. Similarly, the spin–orbit energy splitting for the 5s5p 3P+ level of Sr is about 0.001 Hartree. Given the close proximity to the 5s4d 1D− state which has a binding energy that is only 0.016 au smaller, one could easily see the polarizabilities of the 3P+ spin–orbit states differing by 10%, again leading to a difference of 10% in the Cn values. The possible impact of spin–orbit effects was a primary factor in deciding not to extend the calculations of the heavier caesium and barium atoms. The present results are best regarded as giving a set of average dispersion coefficients. The differences in dispersion coefficients involving spin–orbit doublets could be magnified if the sum rules contain near degeneracies in some of the energy denominators. Taking the present calculations of the dispersion coefficients to the next level of accuracy would require properly relativistic structure calculations.

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