RESEARCH ARTICLE

Long range dispersion interactions of the low lying states of Mg with H, He, Ne, Ar, Kr and Xe

J. Mitroy* and J.Y. Zhang

Faculty of Technology, Charles Darwin University, Darwin, Australia

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The dispersion coefficients for the van der Waals interactions for the low lying states of magnesium (3s2 1S0, 3s3p 3P0, 3s3p 1P0, 3s4s 1S0, 3s4s 1S0, 3s3d 3D0 and 3s3d 1D0) interacting with H, He, Ne, Ar, Kr and Xe are determined using sum rules of reduced matrix elements over pseudo-state representations of the atomic excitation spectra. The sets of transition matrix elements were taken from previous investigations of the van der Waals interactions of the Mg2 dimer and an investigation of the van der Waals interaction for alkali atoms interacting with rare gases.

Keywords: van der Waals; dispersion; MgH

1. Introduction

Recently a formalism [1] was presented that allows the van der Waals interaction between two atoms [2,3], e.g.

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

(1)

to be computed in a relatively straightforward manner. The $C_n$ parameters in Equation (1) are the dispersion coefficients while $R$ is the distance between the two nuclei.

In earlier works, the dispersion coefficients for ground and excited states of alkali atoms interacting with atomic hydrogen, helium and the heavier rare gases were presented [1,4]. The present work extends this series of calculations to give the dispersion coefficients for the low lying states of the magnesium atom interacting with a series of atoms, namely the hydrogen atom and the rare gases.

One of the main applications of this work lies in the area of pressure broadening and shifts [5–7]. The theory of spectral line broadening relies on an accurate description of the potential curves between the two states undergoing the transition, and the perturbing atom. The size of the dispersion parameters has a major influence upon the broadening since many of the collisions occur at large impact parameters. A number of investigations of the pressure broadening of magnesium atoms immersed in rare gas buffer gases have been performed [8–13]. Another area of application occurs because the MgH molecule is astrophysically important [14–16] with much recent activity in the analysis of brown dwarf stars [17–23]. All dispersion coefficients are reported in atomic units (au).

2. Theoretical overview

The approach used to generate the dispersion coefficients is based on the work of Dalgarno who originally derived expressions in terms of oscillator strength sum rules [2,3]. This reduced the calculation of the $C_n$ parameters for two spherically symmetric atoms to sums over the products of the absorption oscillator strengths (originating in the atomic states of interest) 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 [1,24]. 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 \( L > 0 \) [1].

The most time consuming part of any calculation involves the accumulation of lists of reduced transition matrix elements for the atomic states. This involves a series of long calculations to generate the wave functions of all the physical and pseudo-states. Once this has been completed, it is then straightforward to use the formalism outlined in Zhang and Mitroy [1] to process the lists of matrix elements and compute the dispersion coefficients.

The CI calculations used to generate the physical and \( L^2 \) pseudo states of magnesium were very similar to those used to determine the dispersion parameters of the Mg ground state and the metastable \( ^3P^o \) state [24–27]. One difference between the present calculations and the earlier calculations [24–26] is that the orbital basis is somewhat larger [27]. There were a total of 156 valence orbitals with a maximum orbital angular momentum of \( \ell = 6 \). The radial dependence of the orbitals were described by a mixture of Slater-type orbitals (STOs) and Laguerre-type orbitals (LTOs). [24,25] The number of active orbitals for \( \ell = 0 \rightarrow 6 \) were 23, 23, 25, 30, 20, 20 and 15, respectively. The wave function for the \( 1s^22s^22p^6 \) core was taken from a neutral Mg ground state Hartree–Fock (HF) wave function computed by a program written by one of the authors (JM) [28] using a \((9s,5p)\) STO basis based on the values in the Clementi and Roetti compilation [29]. Some \( \ell = 0 \) valence orbitals were generated from the STOs used for the core, but all the other orbitals were written as LTOs due to the superior linear dependence properties of LTO basis sets. The use of the large orbital basis resulted in wave functions and energies for the low lying states that were close to convergence. The length of the CI expansions for the different states ranged from 1600–5000.

The direct and exchange interactions of the valence electrons with the HF core were calculated exactly. A semi-empirical polarization potential, including both one-body and two-body terms, was also added to the core potential. The cutoff parameters of the polarization potential were initially tuned to the experimental energies of the low lying states of Mg\(^+\). Some additional small adjustments to the cutoff parameters were made for some symmetries by tuning the Mg binding energies to experiment. The model potential used reproduced the energies of the low lying Mg spectrum with a maximum discrepancy of \( 1.5 \times 10^{-4} \) Hartree [27]. The expectation values of the multipole operators were calculations using the length form of the multipole operators with core polarization corrections [24,27,30,31].

The transition data for hydrogen were taken from a pseudo-state representation of the hydrogen spectrum [24,32–34] 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 exact energies and polarizabilities for the low lying states of helium [1,35].

The pseudo-oscillator strength distributions for the heavier rare gases came from two sources. The dipole transitions data were taken from compilation of Kumar and Meath [36–37] which use high quality experimental data such as refraction index information to constrain the distribution. The distributions of Mitroy and Zhang [4] 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 [4,38–42].

3. Results

3.1. Dispersion coefficients for the Mg ground state

The dispersion coefficients of the Mg \( 3s^2 \ 1S^e \) ground state are given in Table 1 and compared with the data in the Standard and Certain (SC) compilation [43].

Standard and Certain reported lower and upper limits to the possible dispersion coefficients. These limits were determined by constructing \( f \)-value distributions using a combination of experimental and theoretical information about polarizabilities, sum rules and transition energies to give bounded estimates of the polarizabilities and thus the dispersion coefficients using Pade approximates [43,44].

It can be seen from the table that the present dispersion coefficients in every case lie between the lower and upper bounds specified in the SC compilation. In some cases the bounds are not particularly stringent. For example, the bounds for the \( C_{10} \) coefficient for Ne, Ar, Kr and Xe allow a variation of 20–30\% . The good agreement is a bit of a surprise since the \( C_8 \) and \( C_{10} \) coefficients for alkali-rare gas interactions were often larger than the upper bounds given by SC [4]. The probable cause of the problem are the SC alkali atom oscillator strength distributions for the higher multipoles. The SC quadrupole and octupole pseudo-oscillator strength distributions for the heavier rare gases tend to result in \( C_8 \) and \( C_{10} \) values (for the homo-nuclear rare gas dimers) that are compatible with modern estimates [4,39,42].
One of us (JM) has previously reported the dispersion coefficients of ground state magnesium with H and He [45] using essentially the same methods as used here. The largest differences of this earlier calculation with the present work occur for the C\textsubscript{8} coefficient. The earlier values are 2560 au for Mg–H and 886.4 for Mg–He. These are only 0.3\% larger than the present values. There has also been a large many body perturbation theory calculation of Mg–H giving C\textsubscript{6} = 57.8\pm 0.6 au [18,46]. The present value is only 0.2 au smaller but within the quoted uncertainties.

3.2. Dispersion coefficients for the 1,3\textsuperscript{P}o excited states

The dispersion coefficients of the Mg 3\textit{s}3\textit{p} 1,3\textsuperscript{P}o excited states are given in Table 2. There are two obvious trends in the table. The first is the tendency for the dispersion coefficients to get larger as the rare gas atom increases in size. The other trend is for the dispersion constants for the singlet states to be larger than the corresponding triplet state. This is expected since the polarizabilities of the 3\textit{s}3\textit{p} 1\textsuperscript{P}o state are larger than the polarizabilities of the 3\textit{s}3\textit{p} 3\textsuperscript{P}o state [27]. For example, the static dipole polarizability of the 3\textit{s}3\textit{p} 1\textsuperscript{P}o state was 293.1 a\textsubscript{0}\textsuperscript{3} while the static dipole polarizability of the 3\textit{s}3\textit{p} 3\textsuperscript{P}o was 101.5 a\textsubscript{0}\textsuperscript{3}.

Estimates of the 3\textit{s}3\textit{p} 3\textsuperscript{P}o dispersion coefficients with atomic hydrogen using combination rules were made by Skory et al. [18] in a recent investigation of the properties of the MgH molecule [18–21]. Skory et al. used the same combination rules for the \Sigma and \Pi states. This is not really justified since the angular factors multiplying the oscillator strength sum rules

Table 1. The dispersion coefficients (in au) between the Mg 3\textit{s} ground state and the hydrogen and rare gas atoms. The numbers in the square brackets denote powers of ten.

<table>
<thead>
<tr>
<th>System</th>
<th>(C_6)</th>
<th>(C_8)</th>
<th>(C_{10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>57.59</td>
<td></td>
<td>1.220 [5]</td>
</tr>
<tr>
<td>H (SC)</td>
<td>57.4–58.5</td>
<td>2490–2660</td>
<td>1.15–1.29 [5]</td>
</tr>
<tr>
<td>He</td>
<td>21.45</td>
<td>884.0</td>
<td>3.933 [4]</td>
</tr>
<tr>
<td>Ne</td>
<td>42.18</td>
<td>1844</td>
<td>8.638 [4]</td>
</tr>
<tr>
<td>Ne (SC)</td>
<td>41.5–44.3</td>
<td>1700–1910</td>
<td>7.35–9.05 [4]</td>
</tr>
<tr>
<td>Ar</td>
<td>159.8</td>
<td>7723</td>
<td>3.974 [5]</td>
</tr>
</tbody>
</table>

Table 2. The dispersion coefficients (in au) between the 3\textit{s}3\textit{p} 1,3\textsuperscript{P}o states of Mg and the H and rare gas ground states. The numbers in the square brackets denote powers of ten.

<table>
<thead>
<tr>
<th>System</th>
<th>(C_6)</th>
<th>(C_8)</th>
<th>(C_{10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3\textit{s}\textit{p}–He \Sigma)</td>
<td>77.75</td>
<td>1.052 [4]</td>
<td>1.445 [6]</td>
</tr>
<tr>
<td>(3\textit{s}\textit{p}–He \Pi)</td>
<td>43.41</td>
<td>995.3</td>
<td>4.200 [4]</td>
</tr>
<tr>
<td>(3\textit{s}\textit{p}–Ne \Sigma)</td>
<td>150.8</td>
<td>2.078 [4]</td>
<td>2.904 [6]</td>
</tr>
<tr>
<td>(3\textit{s}\textit{p}–Ar \Pi)</td>
<td>337.2</td>
<td>1.007 [4]</td>
<td>4.883 [5]</td>
</tr>
<tr>
<td>(3\textit{s}\textit{p}–Kr \Sigma)</td>
<td>939.4</td>
<td>1.313 [5]</td>
<td>1.894 [7]</td>
</tr>
<tr>
<td>(3\textit{s}\textit{p}–Kr \Pi)</td>
<td>505.4</td>
<td>1.635 [4]</td>
<td>8.461 [5]</td>
</tr>
<tr>
<td>(3\textit{s}\textit{p}–Xe \Sigma)</td>
<td>1529</td>
<td>2.159 [5]</td>
<td>3.192 [7]</td>
</tr>
<tr>
<td>(3\textit{s}\textit{p}–Xe \Pi)</td>
<td>806.7</td>
<td>2.995 [4]</td>
<td>1.711 [6]</td>
</tr>
</tbody>
</table>

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3.2. Dispersion coefficients for the 3\textsuperscript{P}o excited states

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3.3. Other excited states

The dispersion coefficients involving the Mg 3s4s $^{1,3}S^e$ and Mg 3s3d $^{1,3}D^e$ excited states with the hydrogen and rare gas ground states are given in Tables 3 and 4. Table 3 reveals that the singlet Mg 3s4s excited state has larger dispersion coefficients than the triplet Mg 3s4s state. This was predictable given that the dipole and quadrupole polarizabilities of the singlet state are larger than the triplet state [27].

The relative size of the singlet and triplet dispersion coefficients are reversed for the 3s3d states listed in Table 4. In this case the polarizabilities of the 3s3d $^{3}D^e$ state are larger than the polarizabilities of the 3s3d $^{1}D^e$ state [27].

4. Summary

The van der Waals coefficients between low lying excited states of magnesium with the rare gases or atomic hydrogen have been determined using sum rules over oscillator strengths and transition moments.
There have been a number of previous investigations of the potential surfaces of these systems [15,18,47–57]. Most of these investigations have been concerned with the short range form of the potential surface in the vicinity of the potential minimum. The present set of dispersion coefficients can be used to extend the existing short-range potential curves to infinite nuclear separation.

The accuracy of the dispersion coefficients involving the Mg ground state should be about 2% for $C_6$, with larger uncertainties in the values of $C_8$ and $C_{10}$ for the heavier rare gases. Comparisons of Mg polarizabilities and Mg–Mg dispersion coefficients with MBPT calculations [27] reveal a very high degree of agreement. For example, the difference with MBPT values for $C_6$, $C_8$, and $C_{10}$ are only 0.3%, 0.02% and 2%, respectively [27,58]. The rare gas pseudo-oscillator strengths for the dipole case are expected to give moments that are accurate at the 1% level [36,37]. Accordingly, an overall uncertainty of about 2% for the $C_6$ values involving the Mg ground state seems reasonable. The uncertainties in $C_8$ and $C_{10}$ for the ground state are larger mainly due to the uncertainties in the rare gas quadrupole and octupole oscillator strength distributions [4].

The uncertainties in the dispersion coefficients for the excited states are larger since there is less precise information with which to validate the underlying CI calculations [27]. For example, the only polarizabilities for which large scale calculations (apart from those using the present wave functions) have been done is the ground state [27,58]. Also, the CI energy differences between the excited states are more susceptible to individual errors in the excited state energies than are the energy differences involving the ground state.

References