Long range interactions between like homonuclear alkali metal diatoms
Jason N. Byrd,1 Robin Côté,1 and John A. Montgomery, Jr.1
Department of Physics, University of Connecticut, Storrs, CT 06269

Long range electrostatic and van der Waals coefficients up to terms of order \( R^{-8} \) have been evaluated by the sum over states method using \textit{ab initio} and time dependent density functional theory. We employ several widely used density functionals and systematically investigate the convergence of the calculated results with basis set size. Static electric moments and polarizabilities up to octopole order are also calculated. We present values for \( \text{Li}_2 \) through \( \text{K}_2 \) which are in good agreement with existing values, in addition to new results for \( \text{Rb}_2 \) and \( \text{Cs}_2 \). Interaction potential curves calculated from these results are shown to agree well with high level \textit{ab initio} theory.

I. INTRODUCTION

The long range interactions between atom-diatom and diatom-diatom systems at low densities and cold temperatures is important in many areas of atomic and molecular physics. Applications may be found in precision spectroscopy,1 condensed matter physics,2 as well as in the study3−5 and control6 of chemical reactions. In the study of low density diatomic collisions, interactions at long range play a critical role in the reaction process.7 The weakness of the long range intermolecular interaction compared to the chemical bond and the range of nuclear coordinates necessary to model a long range potential energy surface (PES) suggests that it is advantageous to consider modeling the intermolecular potential in other ways than brute force \textit{ab initio} quantum chemical calculations.

In the limit where the wavefunction overlap between two interacting monomers is negligible, the interaction potential between them can be expanded in a van der Waals series, where the interaction energy can be broken into three distinct components

\[ E_{\text{int}} = E_{\text{el}} + E_{\text{ind}} + E_{\text{disp}}. \]  

(1)

Here \( E_{\text{el}} \), \( E_{\text{ind}} \) and \( E_{\text{disp}} \) are the permanent electrostatic, induction (permanent-induced electrostatic) and dispersion energies and can each be written in an asymptotic series

\[ E_{LR} = \sum_n V_n R^{-n}. \]  

(2)

These contributions to the long range interaction energy can be calculated in several ways. In this work we expand the interaction operator in terms of multipole moments8 and then calculate the interaction energy using first and second order Rayleigh-Schrödinger perturbation theory.

Isotropic dispersion interactions between \( \text{Na}_2 \) and \( \text{K}_2 \) pairs have been previously studied using the London formula9 and time dependent density functional theory (TD-DFT)10−11 Spelsberg et al.12 have calculated van der Waals coefficients including anisotropic corrections using valence full configuration interaction (VFCI) theory for \( \text{Li}_2 \), \( \text{Na}_2 \) and \( \text{K}_2 \). Also recent work by Kotochigova13 has calculated the isotropic van der Waals interaction for \( \text{KRb} \) with leading order anisotropic corrections. In this paper we present results for the van der Waals interactions between pairs of ground state homonuclear alkali metal diatoms, through order \( R^{-8} \), including anisotropic corrections. In Sec. II an outline of the sum over states method of calculating van der Waals coefficients is presented, followed by a discussion of the electronic structure calculations done to obtain the van der Waals coefficients in Sec. III. We conclude in Sec. IV with a discussion of our results. The extension to heteronuclear alkali diatomic van der Waals interactions will be presented in subsequent publications.

II. ANISOTROPIC LONG-RANGE INTERACTIONS

In the Born-Oppenheimer approximation, the interaction between two linear molecules can be expanded in a

![Figure 1: Basis set convergence of the octopole static polarizability values for Na2 evaluated using several \textit{ab initio} and DFT methods.](image-url)

\( n \) (n-aug-def2-QZVPP)
TABLE I. Unique calculated dispersion and induction van der Waals coefficients, $W_{nL_1L_2M}$, for ground state Na$_2$ using selected ab initio and DFT methods. The RMS deviations are relative to previous theoretical results. All calculations are performed at the experimental equilibrium bond length.

| n L$_1$ L$_2$ M | CIS | TD-HF | VWN | B3LYP | CAMB3LYP | B3PW91 | PBE0 |
|----------------|-----|-------|-----|-------|-----------|--------|------|
| Dispersion     |     |       |     |       |           |        |      |
| 6 0 0 0        | 8.304(3) | 4.679(3) | 4.094(3) | 3.697(3) | 3.654(3) | 4.216(3) | 4.073(3) |
| 6 2 0 0        | 1.192(4) | 5.465(2) | 4.985(2) | 5.408(2) | 5.092(2) | 5.984(2) | 5.487(2) |
| 6 2 2 0        | 5.442(2) | 2.128(2) | 2.030(2) | 2.633(2) | 2.363(2) | 2.842(2) | 2.470(2) |
| 6 2 2 1        | -1.209(2) | -4.728(1) | -4.511(1) | -5.851(1) | -5.231(1) | -6.315(1) | -5.489(1) |
| 6 2 2 2        | 1.512(1) | 5.910(0) | 5.639(0) | 7.314(0) | 6.564(0) | 7.893(0) | 6.861(0) |
| %RMS           | 44.6 | 5.8  | 2.8  | 5.5   | 6.1    | 1.4    | 2.3  |

| Induction      |     |       |     |       |           |        |      |
| 8 0 0 0        | 9.397(5) | 6.569(5) | 5.020(5) | 5.491(5) | 4.923(5) | 6.035(5) | 5.777(5) |
| 8 2 0 0        | 4.593(5) | 2.789(5) | 2.261(5) | 3.183(5) | 2.608(5) | 3.324(5) | 3.082(5) |
| 8 2 2 0        | 1.242(5) | 6.206(4) | 5.249(4) | 8.974(4) | 6.941(4) | 9.124(4) | 8.025(4) |
| 8 2 2 1        | -1.687(4) | -8.525(3) | -7.200(3) | -1.241(4) | -9.553(3) | -1.262(4) | -1.109(4) |
| 8 2 2 2        | 4.759(2) | 3.091(2) | 2.541(2) | 5.072(2) | 3.593(2) | 5.198(2) | 4.481(2) |
| 8 4 0 0        | 2.388(4) | 1.116(4) | 9.514(3) | 1.607(4) | 1.340(4) | 1.376(4) | 1.253(4) |
| 8 4 2 0        | 1.439(4) | 5.778(3) | 5.170(3) | 1.029(4) | 8.154(3) | 8.760(3) | 7.528(3) |
| 8 4 2 1        | -1.906(3) | -7.647(2) | -6.843(2) | -1.362(3) | -1.080(3) | -1.157(3) | -0.951(2) |
| 8 4 2 2        | 9.713(1) | 3.895(1) | 3.484(1) | 6.941(1) | 5.507(1) | 5.862(1) | 5.047(1) |
| %RMS           | 22.1 | 7.3  | 8.0  | 5.5   | 8.6    | 3.0    | 4.3  |

The interaction energy is rotationally invariant, it may be expanded in terms of multipole operators $Q_{lm} = \sum \hat{r}_i r_i^l C_{lm}(\hat{r}_i)$, where $C_{lm}(\hat{r}_i)$ is a Racah spherical harmonic. Using first- and second-order perturbation theory, Mulder et al. express the coefficients $E_{L_1L_2M}(R)$ in terms of the separated monomer transition moments. When this is done, the interaction energy may be written as

$$E_{\text{int}}(R, \phi_1, \phi_2, \phi_3) = \sum_{L_1L_2M} V_{L_1L_2M}^{(1,2)}(R) P_{L_1}^M(\cos \theta_1) P_{L_2}^M(\cos \theta_2) \cos M(\phi_1 - \phi_2),$$

where

$$P_{L_1}^M(\cos \theta_1) = \sum_{M=0}^{\min(L_1, L_2)} \eta^M_{L_1L_2L} (\cos \theta_1)^M,$$

$$V_{L_1L_2M}^{(1,2)}(R) = \sum_{L_1L_2M} V_{L_1L_2M}^{(1)}(R) = \left[ (L_1 - M)(L_2 - M) \right]^{1/2},$$

(3)

Here the first-order contribution

$$V_{L_1L_2M}^{(1)}(R) = W_{nL_1L_2M} R^{-n} \delta_{L_1+L_2+n},$$

(4)

(5)
| System | Method  | $r_c$ (a.u.) | $\alpha_2$ (a.u.) | $\alpha_4$ (a.u.) |
|--------|---------|--------------|------------------|------------------|
| Li$_2$ | B3PW91  | 5.051        | 268.4            | 170.0            |
|        | PBE0    | 5.051        | 262.4            | 168.7            |
|        | Ref. 18 | 5.051        | 305.2            | 162.4            |
|        | Ref. 12 | 5.051        | 297.7            | 161.5            |
| Na$_2$ | B3PW91  | 5.818        | 352.2            | 206.2            |
|        | PBE0    | 5.818        | 338.7            | 203.7            |
|        | Ref. 18 | 5.818        | 378.5            | 162.4            |
|        | Ref. 12 | 5.818        | 370.1            | 201.6            |
| K$_2$  | B3PW91  | 7.416        | 714.6            | 301.5            |
|        | PBE0    | 7.416        | 676.2            | 395.4            |
|        | Ref. 18 | 7.416        | 708.2            | 359.6            |
|        | Ref. 12 | 7.379        | 677.8            | 363.1            |
| Rb$_2$ | B3PW91  | 7.956        | 830.2            | 453.6            |
|        | PBE0    | 7.956        | 785.8            | 448.3            |
|        | Ref. 18 | 7.956        | 789.7            | 405.5            |
| Cs$_2$ | B3PW91  | 8.284        | 1096.0           | 577.8            |
|        | PBE0    | 8.284        | 1032.9           | 568.3            |

**TABLE II.** Static dipole polarizability values for the $X^1\Sigma_g^+$ homonuclear alkali diatoms calculated at the experimental equilibrium bond length.

$$W_{nL_1L_2M}^{(1)} = -(1)^{L_1+M}(2 - \delta_{M,0}) \frac{(L_1 + L_2)!}{(L_1 + M)!(L_2 + M)!} \times \langle 0|Q_{L_0}^{0}|0\rangle \langle 0|Q_{L_0}^{0}|0\rangle (8)$$

is due to the electrostatic interaction and the second-order terms

$$V_{L_1L_2M}^{(2)}(R) = - \sum_{l_i'j_i'j'_i} C_n^{l_i'l_i:j_i'j'_i} R^{-n} \delta_{l_1l_1'} \delta_{l_2l_2'} \delta_{l_{2}+l_2'+2n} (9)$$

contain contributions from dispersion and induction. The sum implies that $k_1 + k_2 \neq 0$ and $\epsilon_{k_1}$ is the energy of the $k_1$th state. The $C_n^{l_i'l_i:j_i'j'_i}$ coefficient is a scalar coupling term given by

$$C_n^{l_i'l_i:j_i'j'_i} = (1)^{l_1+l_2}((2L_1 + 1)!(2L_2 + 1)!)^{1/2} \times \left[ \frac{(2l_1 + 2l_2 + 1)!(2l'_1 + 2l'_2 + 1)!}{(2l_1)!(2l'_1)!(2l_2)!(2l'_2)!} \right]^{1/2} \sum L \eta_{L_1L_2}^M$$

$$\times (l_1 + l_2; l'_1 + l'_2|0) \left\{ \begin{array}{c} l_1 \\ l_2 \\ l'_1 \\ l'_2 \\ L_1 \\ L_2 \\ L \end{array} \right\}, (10)$$

Table III. Comparison of theoretical isotropic $V_6$ van der Waals coefficients.

| System | Li$_2$   | Na$_2$   | K$_2$   |
|--------|----------|----------|---------|
| B3PW91 | 2.649(3) | 4.216(3) | 1.242(4)|
| PBE0   | 2.593(3) | 4.073(3) | 1.185(4)|
| SAOP   | 4.460(3)$^a$ | 1.106(4)$^b$ | |
| London$^c$ | 3.74(3) | 1.186(4) | |
| Valence FCI$^d$ | 2.730(3) | 4.181(3) | 1.039(4) |

$^a$ Ref. 10  
$^b$ Ref. 11  
$^c$ Ref. 12  
$^d$ Ref. 13

It is convenient in practice to collect all terms with the same $R$-dependence in Eq. 10 into a single expression

$$V_{L_1L_2M}^{(2)}(R) = - \sum_n \frac{W_{nL_1L_2M}^{(2)}}{R^n}. (15)$$

The dispersion and induction contributions to Eq. 15 are calculated separately as

$$W_{nL_1L_2M}^{(2)} = W_{nL_1L_2M}^{(2,DIS)} + W_{nL_1L_2M}^{(2,IND)} (16)$$

and presented in Tables II and V.
### III. ELECTRONIC STRUCTURE CALCULATIONS

Transition moment calculations for use in the evaluation of Eq. [12] were done for the homonuclear alkali metal diatoms Li$_2$, Na$_2$, K$_2$, Rb$_2$, and Cs$_2$ in the $X^1\Sigma^+_g$ ground state using a locally modified version of the GAMESS$^{19,20}$ quantum chemistry program package. All calculations have been performed at the experimental equilibrium bond distances. The number of excited states included in the sum in Eq. [10] is taken to be the total number of virtual orbitals present. Tests were performed to ensure convergence of the calculated TD-DFT transition moments with respect to the grid size. The grid employed in production calculations uses 155 radial points for all atoms, and prunes from a Lebedev grid whose largest size is 974, thus using about 71,000 grid points/atom (the JANS=2 grid in GAMESS).

To provide consistent results for all the alkali metals, the Karlsruhe def2-QZVPP$^{21}$ basis sets were chosen for this work. The def2 basis sets are available for almost the entire Periodic Table and are well-known for their robustness and their excellent cost-to-performance ratio in large-scale Hartree-Fock and density functional theory (DFT) calculations. The def2-QZVPP basis sets for the alkali metals contain spdf basis functions with two polarization functions. For the row five and lower atoms, the inner-core electrons are replaced by an effective core potential (ECP) to reduce the number of electrons included in the correlation treatment and to account for scalar-relativistic effects. The ECP-22$^{22}$ and ECP-46$^{22}$ Stuttgart pseudopotentials were used for Rb and Cs respectively. These ECP definitions leave the sub-valence $s$ and $p$ electrons free, which are known to contribute the most to core-valence correlation energies$^{23}$ in alkaline systems. In the transition moment calculations presented here, core-valence correlation is accounted for implicitly within the DFT formalism.

When examining the effects of basis set convergence of the van der Waals coefficients it is convenient to first look at the convergence of the multipole polarizability defined as

$$\alpha_{ll'm} = 2 \sum_k \frac{\langle 0|Q_{lm}|k\rangle\langle k|Q_{l'-m'}|0\rangle}{\epsilon_k - \epsilon_0}.$$  \hspace{1cm} (17)

The octopole polarizability terms $\alpha_{300}$ are the most sensitive to the effects of higher angular momentum functions in the basis set, and were therefore used to assess the convergence of our results with respect to basis set size. Test calculations including a sequence of $g$ basis functions ranging from valence to diffuse indicated that there was no need to add higher angular momentum functions to the def2 basis sets. The effects of adding additional sets of diffuse even tempered spdf basis functions can be seen in Fig. [1]. It was found that two additional sets of diffuse functions was necessary to achieve accurate results for our test case of Na$_2$. For a subset of the DFT functionality considered here, the addition of a third set of diffuse functions was investigated and found to contribute little to the calculated polarizabilities. The def2-QZVPP basis sets for K, Rb and Cs include an additional set of diffuse function by definition and so only required a single additional set of diffuse basis functions. We note that the dipole polarizability, and hence the $V_6$ van der Waals coefficients, are essentially converged using the unmodified def2 basis set. A similar procedure was recently used by Rappoport and Furche$^{24}$ to optimize the Karlsruhe def2 basis sets for molecular property calculations.

Using the double augmented basis set (d-aug-def2-QZVPP) described above two $ab\text{ initio}$ methods were considered for our test case Na$_2$, configuration interaction singles$^{29,30}$ (CIS) and time dependent Hartree-Fock$^{29,31}$ (TD-HF) theory. Additionally we used time dependent density functional theory (TD-DFT)$^{29,31}$ to evaluate excitation energies and multipole transition moments. The results of the $ab\text{ initio}$ and TD-DFT calculations are compared to those of Spelsberg and Meyer$^{12}$ in Table [I]. Despite the success$^{12}$ in describing the van der Waals interaction of H$_2$, CIS significantly over estimates the dispersion and induction van der Waals interaction. This is not unexpected as CIS is known not to obey the Thomas-Reiche-Kuhn dipole sum rule because it overestimates the transition moments. An additional source of error in CIS is the overestimation of excitation energies that results from the use of canonical Hartree-Fock virtual orbital energies. The overall performance of TD-DFT compared to the results of Spelsberg and Meyer$^{12}$ appears quite good. Upon examining the results of Table [I] we have chosen the B3PW91 and PBE0 functionals for use in the rest of this work due to the consistent accuracy for both dispersion and induction interactions.

The electric quadrupole moment used to calculate $V_5$ was evaluated using the finite field method using

| $n L_1 L_2 M$ | Li$_2$ | Na$_2$ | K$_2$ | Rb$_2$ | Cs$_2$ |
|--------------|-------|-------|------|-------|-------|
| $Q_{20}$     | 10.74 | 10.52 | 15.68| 10.06 | 27.85 |
| 5220         | 6.921(2)| 6.640(2)| 1.475(3)| 1.548(3)| 1.912(2)|
| 5221         | −1.538(2)| −1.476(2)| −3.278(2)| −3.439(2)| −4.248(2)|
| 5222         | 9.612(0)| 9.223(0)| 2.049(1)| 2.149(1)| 2.655(1)|

TABLE IV. Electrostatic van der Waals coefficients, $W_n^{(1)}_{k_1 k_2 M}$, for the ground state alkali dimers Li$_2$, Na$_2$, K$_2$, Rb$_2$ and Cs$_2$ calculated at the CCSD(T) level of theory using the finite field method.
CCSD(T). Core-valence contributions are accounted for by including the inner valence $s$ and $p$ electrons in the correlation treatment. For consistency the n-def2-QZVPP basis sets defined above were used. Comparisons with the results of Harrison and Lawson for Li$_2$, Na$_2$, and K$_2$ show that this choice of basis set provides reliable results. In Table IV we show our calculated quadrupole moment and $V_5$ van der Waals coefficients for the homonuclear alkali diatoms including new results for Rb$_2$ and Cs$_2$.

IV. NUMERICAL RESULTS AND DISCUSSION

As noted above, the Karlsruhe def2 basis sets replace the inner shell electrons of rubidium and cesium with an effective core potential. In order to assess the effect of replacing the inner-core electrons in heavy atoms by a pseudopotential, we have performed calculations of the $K_2$ van der Waals coefficients using the Stuttgart ECP and basis set, and made comparisons with our all-electron calculations using the def2 basis set. The Stuttgart $sp$ ECP basis set was uncontracted, and to ensure that the basis set was fully saturated the most diffuse five $p$ exponents were added as $d$ functions and the subsequent most diffuse four $d$ exponents were added as $f$ functions. Using this basis and ECP, it was found that the difference between the ECP and all-electron def2 results were negligible. An important consideration for any van der Waals study is that of the dipole polarizability of the individual molecules as the leading dispersion interaction term $V_6$ is proportional to the product of polarizabilities. Using our n-aug-def2-QZVPP basis sets with the B3PW91 and PBE0 DFT functionals we have calculated the dipole, quadrupole and octopole polarizabilities for all the alkali diatoms considered in this work. In Table III the dipole polarizabilities are presented with several other existing theoretical results in comparison. The calculated higher order polarizabilities can be found in the supplemental material. Because the polarizability is very sensitive to the diatomic bond distance near equilibrium we have chosen to perform all calculations at the experimental equilibrium bond length, rather than at the optimized geometry for each different level of theory. As a consequence, there will be small deviations in the parallel components of the calculated polarizability at a particular level of theory compared to what would be found at the optimized geometry. Therefore, our calculated values for the perpendicular dipole polarizability ($\alpha_{111}$) agrees better with the existing theoretical results than the parallel polarizability ($\alpha_{110}$). For the higher order polarizabilities, the only available values come from Spelsberg et al. The total polarizability RMS error for Li$_2$, Na$_2$ and K$_2$ is 8.7%, 6.7% and 9.5% and 7.5%, 5.1% and 6.9% for B3PW91 and PBE0 respectively.

Often neglected, the leading order term in the van der Waals expansion for homonuclear alkali diatoms is the electrostatic $V_5$ quadrupole-quadrupole interaction. This leads to a repulsive interaction potential for a significant portion of the interaction phase space with a long range barrier; for the case of Na$_2$ this barrier has a maximum height of $\sim 13\text{cm}^{-1}$ for the co-linear orientation ($\theta_1 = \theta_2 = 0$). There are however orientations of approaching pairs of molecules for which no barriers are found. For example, this was seen for Na$_2$ and K$_2$ by Zemke et al as well as for the related systems of K$_2$+Rb$_2$ and Rb$_2$+Cs$_2$ where the lowest energy reaction path was calculated ab initio and indeed was found to be barrier less. To illustrate the effect of including the $V_5$ electrostatic term as well as the higher order $V_6$ terms, the results of the London approximation given by Zemke et al are compared in Fig. 2 to the TD-DFT/PBE0 induction and dispersion coefficients reported above for the co-linear orientation. As a comparison, the potential curve was also calculated using the CCSD(T)-F12a (explicitly correlated CCSD(T)) level of theory. As can be seen in Fig. 2 the inclusion of $V_5$ greatly improves the long range representation of the potential, while the higher order van der Waals terms are necessary to describe the interaction as the molecule separation decreases. With the inclusion of the higher order terms reported in this work, the van der Waals surface matches the barrier height and molecule separation to a few percent.

In a cold ($J = 0$) ensemble with no external field the rotationally averaged electrostatic $V_5$ van der Waals coefficient evaluates to zero. For this case the leading order term in the van der Waals series is the isotropic $V_6$ dispersion interaction. We compare our calculated $V_6$ coefficients to existing theoretical results in Table III. For the case of Li$_2$ it can be seen that B3PW91 performs well, which is also true from Table III for the case of Na$_2$. For the heavier $K_2$ we find that PBE0 performs marginally better for $V_6$. In Table IV all the calculated van der Waals coefficients including all anisotropic contributions for Li$_2$...
| $n L_1 L_2 M$ | B3PW91 | PBE0 | B3PW91 | PBE0 | B3PW91 | PBE0 | B3PW91 | PBE0 | B3PW91 | PBE0 |
|-------------|--------|------|--------|------|--------|------|--------|------|--------|------|
| **Dispersion** | | | | | | | | | | |
| 6 0 0 0 | 2.649(3) | 2.593(3) | 1.242(4) | 1.185(4) | 1.600(4) | 1.530(4) | 2.457(4) | 2.334(4) | | |
| 6 2 0 0 | 2.996(2) | 2.836(2) | 1.939(3) | 1.722(3) | 2.652(3) | 2.355(3) | 4.428(3) | 3.925(3) | | |
| 6 2 2 0 | 1.187(2) | 1.086(2) | 9.994(2) | 8.237(2) | 1.442(3) | 1.186(3) | 2.583(3) | 2.133(3) | | |
| 6 2 2 1 | -2.638(1) | -2.414(1) | -2.221(2) | -1.830(2) | -3.205(2) | -2.636(2) | -5.739(2) | -4.740(2) | | |
| 6 2 2 2 | 3.297(0) | 3.017(0) | 2.776(1) | 2.288(1) | 4.006(1) | 3.295(1) | 7.174(1) | 5.925(1) | | |
| %RMS | 2.7 | 3.4 | 8.8 | 6.4 | | | | | |
| **Induction** | | | | | | | | | | |
| 8 0 0 0 | 3.170(5) | 3.075(5) | 2.714(6) | 2.553(6) | 3.928(6) | 3.715(6) | 7.249(6) | 6.792(6) | | |
| 8 2 0 0 | 1.302(5) | 1.236(5) | 1.714(6) | 1.553(6) | 2.615(6) | 2.374(6) | 5.288(6) | 4.762(6) | | |
| 8 2 2 0 | 2.963(4) | 2.717(4) | 5.140(5) | 4.335(5) | 8.191(5) | 6.897(5) | 1.786(6) | 1.499(6) | | |
| 8 2 2 1 | -4.118(3) | -3.771(3) | -7.152(4) | -6.032(4) | -1.132(5) | -9.527(4) | -2.466(5) | -2.068(5) | | |
| 8 2 2 2 | 1.824(2) | 1.629(2) | 3.217(3) | 2.735(3) | 4.558(3) | 3.811(3) | 9.693(3) | 8.080(3) | | |
| 8 4 0 0 | 1.592(3) | 1.698(3) | 9.509(4) | 8.304(4) | 1.801(5) | 1.629(5) | 4.709(5) | 4.216(5) | | |
| 8 4 2 0 | 1.318(3) | 1.284(3) | 6.279(4) | 5.068(4) | 1.247(5) | 1.045(5) | 3.512(5) | 2.933(5) | | |
| 8 4 2 1 | -1.721(2) | -1.680(2) | -8.307(3) | -6.706(3) | -1.653(4) | -1.386(4) | -4.665(4) | -3.896(4) | | |
| 8 4 2 2 | 8.383(0) | 8.254(0) | 4.225(2) | 3.413(2) | 8.456(2) | 7.101(2) | 2.402(3) | 2.007(3) | | |
| %RMS | 4.5 | 5.4 | 7.2 | 5.9 | | | | | |

TABLE V. Unique van der Waals coefficients, $W_{M,nL_1L_2}$, for the ground state alkali dimers Li$_2$, K$_2$ and new results for Rb$_2$ and Cs$_2$ calculated at the TD-DFT level of theory using the B3PW91 and PBE0 functionals. The RMS deviations are relative to previous theoretical results, where applicable.
and $K_2$ are presented. To compare with the results of Spelsberg et al.\textsuperscript{22} it is necessary to recouple their interaction coefficients from the $L_1, L_2, L$ coupling scheme to the $L_1, L_2, M$ coupling scheme used here by the following

$$V_{L_1L_2M} = \sum_L n_{L_1L_2L}^M V_{L_1L_2L}. \quad (18)$$

After recoupling we find our van der Waals coefficients to be in good agreement with those of Spelsberg et al.\textsuperscript{22} Also in Table V are our new results for Rb\textsubscript{2} and Cs\textsubscript{2}. Using the aug-def2-QZVPP basis set and ECP, our calculations for Rb\textsubscript{2} and Cs\textsubscript{2} contain comparable numbers of electrons to the all-electron calculations for Na\textsubscript{2}, and therefore we expect our van der Waals coefficients for these alkali diatoms to be comparably accurate.

V. CONCLUSION

In summary, we have used \textit{ab initio} and TD-DFT methods to calculate excitation energies and transition moments for the homonuclear alkali diatoms Li\textsubscript{2}, Na\textsubscript{2}, K\textsubscript{2}, and Cs\textsubscript{2}. These energies and moments were used in a sum over states calculation of the electrostatic, induction and dispersion van der Waals coefficients as well as static polarizabilities up to third order. The Karlsruhe def2-QZVPP basis sets were augmented with diffuse functions to ensure accurate calculation of the multipole polarizabilities and van der Waals coefficients. Calculated dipole polarizabilities were found to be consistent with other theoretical results, while noting that the polarizability is sensitive to the diatomic bond length.\textsuperscript{18} Van der Waals results for the lighter systems are in good agreement with the existing literature, and suggest errors of a few percent for the new results for Rb\textsubscript{2} and Cs\textsubscript{2}. As such the long range interaction of each alkali diatomic pair can be characterized by a van der Waals series of the form

$$E_{int}(R, \theta_1, \phi_1, \theta_2, \phi_2) = \sum_{n_{L_1L_2M}} \frac{(W_{nL_1L_2M}^{(1)} - W_{nL_1L_2M}^{(2)})}{R^n} \times P_{L_1}^M(\cos(\theta_1))P_{L_2}^M(\cos(\theta_2))\cos(M(\phi_1 - \phi_2)) \quad (19)$$

where the $W_{nL_1L_2M}^{(1,2)}$ coefficients can be taken directly from Tables II and V. We provide a sample FORTRAN program for evaluating Eq. (19) in the supplemental material for the case of Na\textsubscript{2} as described in Fig. 2. The current study suggests that the calculation of the van der Waals expansion coefficients can provide an accurate model of the long range potential surface in alkali dimers.

It is noted that the leading order van der Waals coefficient is the electrostatic $V_5$ quadrupole-quadrupole interaction. This term provides a molecular frame repulsive interaction at long range for a portion of the diatom-diatom phase space. This repulsive interaction will lead to a stabilization of the molecules when confined in a trap. Coupling with an external field can lead to a richer interaction phase space beyond that of the isotropic dispersion interaction.

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Appendix A: Relationship of the sum over states method to the Casimir-Polder formulation

The sum over states formulation of Eq. (11) is not the only way to obtain dispersion interactions as described in Eq. (4). We define the coupled dynamic polarizability as

$$\alpha_{L_1L_2}(\omega) = \sum_{k_{i\neq0}} \frac{\Delta \epsilon_{k_i}}{\epsilon_{k_i} - \omega^2} \quad (A1)$$

where $\Delta \epsilon_{k_i} = \epsilon_{k_i} - \epsilon_0$ is the $k_i$’th excitation energy. Using the identity

$$\frac{1}{a + b} = \frac{2}{\pi} \int_0^\infty \frac{ab}{(a^2 + \omega^2)(b^2 + \omega^2)}d\omega \quad (A2)$$

then Eq. (14) can be rewritten as

$$\frac{2}{\pi} \int_0^\infty \alpha_{L_1}^{(1)}(i\omega)\alpha_{L_2}^{(1)}(i\omega)d\omega \quad (A3)$$

which is the well known Casimir-Polder integral for dispersion interactions between two molecules.

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