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Ultracold Chemistry of Alkali Clusters

Jason N. Byrd, Ph.D.

University of Connecticut, 2013

The calculation of non-covalent interactions of highly polarizable molecules is an outstanding problem in chemistry and physics. Difficulties arise both in accurate treatments of dispersion interactions between molecules and in the evaluation of surfaces of sufficient size for use in further computations. While "gold-standard" calculations using coupled cluster theory with singles, doubles and perturbative triples provides a reliable method for evaluating interactions the computational cost involved in calculating more than a few points of an interaction surface becomes prohibitive for even medium sized molecules. Expanding the long range interaction into a van der Waals series reduces the cost of evaluating a surface to the computation of a few parameters. We describe here the implementation of a new computer program for calculating van der Waals coefficients for arbitrary molecules using the sum over states method. The laboratory-frame transformation of the computed van der Waals surface and the inclusion of rotational state dressing on the surface is derived. Analytic approximations for the interactions of two linear molecules in the presence of a small DC electric field are also derived. Recent achievements in the formation and manipulation of ultracold polar molecules have opened the door to exciting new studies in cold chemical reactions. To characterize the energetics and reaction pathways of trimer and tetramer formation and reactions, we have computed the structure and thermochemistry of the model trimer Li_3 and every X_2Y_2 alkali tetramer through Cs. Related interest in the control of molecular ion reactions is also investigated with recent theoretical results for the rubidium hydroxide reaction presented here.

Ultracold Chemistry of Alkali Clusters

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University of Connecticut

2013

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APPROVAL PAGE

Doctor of Philosophy Dissertation

Ultracold Chemistry of Alkali Clusters

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Chapter 1 Motivation and Overview

The primary purpose of this work is to overview the series of investigations of alkali cluster chemistry performed by the author while in the Côté research group at the University of Connecticut. Included is the specific theory of long range interactions of diatoms [5, 6], with its generalization to arbitrary molecules and the effects of rotational dressing on the long range potential [6]. Also covered are our computational results for the long range interaction between alkali diatoms [3, 5, 6], the prospects [7] and details of alignment and orientation [6] of polar alkali diatoms using external fields as well as the thermochemical and structure calculations of the alkali trimers and tetramers [8–11]. Additional work includes the new investigation of rubidium with small hydrides and a lengthy appendix discussing the computer program implementing the sum over states approach to general long range interactions between molecules.

1.1 Current development in cold chemistry

The many advancements in the study of ultra-cold alkali atoms in the last two decades has strongly motivated concurrent research in cold molecules [12–15]. This motivation has brought forth many different methods for obtaining cold molecules ranging from indirect methods such as Stark and magneto decelerators or buffer gas cooling, which rely on forming molecules, then cooling them using external forces [16, 17] (electric/magnetic dipole moments and quenching collisions with a cryogenic gas), to direct formation methods such as magneto- and controlled photo-association [18–22]. Due to their broad applicability to many different molecules, buffer gas and Stark deceleration cooling methods have seen a strong push in the experimental community [23–29]. While direct cooling of molecules is difficult due to the great number of internal degrees of freedom and energy levels, progress has been made even here [30]. The most progress however comes from the extensions of cold alkali atoms to cold alkali diatomic systems, pioneered by the formation of K_2 [31] and Cs_2 [32, 33]. Since then all other ultracold homonuclear alkali diatoms have been formed via some form of magneto- and/or photo-association. The push to different atomic species to form heteronuclear diatoms has led to the formation and trapping of ground state KRb [34–38] and the formation of RbCs [39–42].

For chemical physics, applications of cold alkali diatoms range from precision spectroscopy [43–46], to the study [37, 47–49] and control [45, 50] of cold chemical reactions. Other areas of physics benefit from the use of polar molecules, such as condensed matter physics [51, 52], and the search for novel quantum gases [53] and phases [54]. Furthermore, dipolar gases in particular have been the subject of much interest from the quantum information community [55–59], and ideas of atom optics (*e.g.* using evanescent wave mirrors [60]) have been generalized to polar molecules [61, 62]. For strictly three-body interactions in the ultracold regime exotic Efimov states have been predicted and measured [63, 64]. The recent achievements in molecular alignment and control [65, 66] may also provide the ability to take advantage of the unique properties and possible control provided by ultracold polar molecules. In addition, there is growing interest in reactions of alkali diatoms to form tetramer structures [10, 11, 67] with reasonable dipole moments and rich molecular structures, which could offer good candidates for quantum computing with dipoles [68].

In each of these applications it is crucial to accurately describe the inter-molecular interactions and energetics. Generally speaking, to understand theoretically the behavior of two or more molecules interacting it is necessary to perform a complete state to state collision calculation, requiring a many dimensional potential energy surface. However this is itself difficult if not entirely intractable. If the systems are restricted to cold temperatures, as found in the examples put forward above, one can notice that the interactions are almost entirely dominated by their long range behavior [69]. Characterizing then the product and reactant energetics in addition to the long range interaction between products can provide a significant amount of information about the reaction process. Computing structures and thermochemistries of molecular complexes can be done using the *ab initio* methods developed by the chemistry and physics community over the past few decades. With care and appropriate methodologies it is indeed possible to achieve thermochemistry accuracies better than the 1 kJoule mol^{-1} (~ 10 cm⁻¹) standard from the chemistry community^{*}. However, because of the weakness of the long range intermolecular forces as compared to the chemical bond, and the range of nuclear coordinates and phase space involved, it is advantageous to consider alternative methods of modeling the intermolecular potential other than *ab initio* quantum chemical calculations. Our own approach to solving the long range problem is described in detail in Chapter 2, with computational examples given in Chapter 3.

^{*}However this theoretical accuracy is well above the experimental precision of 1 GHz or $.03 \text{ cm}^{-1}$ found in modern molecular experiments

Chapter 2

Anisotropic Long Range Molecular Interactions: Theory

A standard approach^{*} to describing the long range interaction potential between two molecules, in the limit that the wavefunction overlap between the molecules is negligible, is to expand the interaction energy into three distinct components,

$$E_{\rm int} = E_{\rm el} + E_{\rm ind} + E_{\rm disp}.$$
(2.1)

Here $E_{\rm el}$, $E_{\rm ind}$ and $E_{\rm disp}$ are the permanent electrostatic, induction (permanentinduced electrostatic) and dispersion energies. Each of these terms can be perturbatively expanded in an asymptotic van der Waals series,

$$E_{\rm LR} = \sum_{n} C_n R^{-n}.$$
(2.2)

The coefficients C_n are in general angular dependent, and can be computed in several ways. In this work, we expand the intermolecular electronic interaction operator in a multipole expansion [71], and then use first- and second-order perturbation theory to calculate the van der Waals coefficients. The the details are covered in the following sections.

^{*}An excellent introductory text on the subject of long range interactions is the book by Stone [70].

2.1 Long range interactions of linear molecules^{*}

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

$$E_{\rm int}(\hat{r}_1, \hat{r}_2, \mathbf{R}) = \sum_{L_1 L_2 L} E_{L_1 L_2 L}(R) A_{L_1 L_2 L}(\hat{r}_1, \hat{r}_2, \hat{R}), \qquad (2.3)$$

where $E_{L_1L_2L}(R)$ are the angular independent radial functions, $\hat{r}_i = (\theta_i, \phi_i)$ are the molecular orientations and $\mathbf{R} = (R, \theta, \phi)$ defines the vector between the molecular centers. As shown by Mulder, van der Avoird, and Wormer [72], if we choose coordinates so that \mathbf{R} is oriented along the z axis, the angular functions may be written as

$$A_{L_1L_2L}(\hat{r}_1, \hat{r}_2, \hat{R}) = \sum_{M=0}^{\min(L_1L_2)} \eta^M_{L_1L_2L} P^M_{L_1}(\cos\theta_1) P^M_{L_2}(\cos\theta_2) \cos M(\phi_1 - \phi_2), \quad (2.4)$$

where

$$\eta_{L_1L_2L}^M = (-1)^M (2 - \delta_{M,0}) (L_1M; L_2 - M | L0) \left[\frac{(L_1 - M)! (L_2 - M)!}{(L_1 + M)! (L_2 + M)!} \right]^{1/2}, \quad (2.5)$$

 $(L_1M; L_2 - M|L0)$ is a Clebsch-Gordon coefficient, and $P_L^M(\cos\theta)$ is an associated Legendre polynomial. Because the interaction energy is rotationally invariant, it may be expanded in terms of multipole operators,

$$Q_{\ell m} = \sum_{i} z_{i} r_{i}^{\ell} C_{\ell m}(\hat{r}_{i}), \qquad (2.6)$$

where the sum is over all charges, z_i is the charge at each *i*'th center, r_i^l is the distance from each *i*'th charge to the center of mass and $C_{lm}(\hat{r}_i)$ is a Racah spherical harmonic

^{*}Text and figures reprinted with permission from [5]. Copywrite 2011 The American Institute of Physics.

[73]. Using first- and second-order perturbation theory, Mulder *et al.* [72, 74] express the coefficients $E_{L_1L_2L}(R)$ in terms of the separated monomer transition moments. When this is done, the interaction energy in Eq.(2.3) may be written as

$$E_{\rm int}(R,\theta_1,\phi_1,\theta_2,\phi_2) = \sum_{L_1L_2} \sum_{M=0}^{\min(L_1,L_2)} V_{L_1L_2M}^{(1)}(R) + V_{L_1L_2M}^{(2)}(R) \times P_{L_1}^M(\cos\theta_1) P_{L_2}^M(\cos\theta_2) \cos M(\phi_1 - \phi_2). \quad (2.7)$$

Here the first-order contribution

$$V_{L_{1}L_{2}M}^{(1)}(R) = W_{nL_{1}L_{2}M}^{(1)} R^{-n} \delta_{L_{1}+L_{2}+1,n},$$

$$W_{nL_{1}L_{2}M}^{(1)} = (-1)^{L_{1}+M} (2 - \delta_{M,0}) \frac{(L_{1}+L_{2})!}{(L_{1}+M)!(L_{2}+M)!} \langle 0_{1} | Q_{L_{1}0} | 0_{1} \rangle \langle 0_{2} | Q_{L_{2}0} | 0_{2} \rangle$$
(2.9)

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

$$V_{L_1L_2M}^{(2)}(R) = -\sum_{\ell_1\ell'_1\ell_2\ell'_2} C_n^{\ell_1\ell'_1L_1;\ell_2\ell'_2L_2;M} R^{-n} \delta_{\ell_1+\ell'_1+\ell_2+\ell'_2+2,n},$$
(2.10)

$$C_n^{\ell_1\ell_1'L_1;\ell_2\ell_2'L_2;M} = \zeta_{L_1L_2M}^{\ell_1\ell_1';\ell_2\ell_2'} \sum_{k_1k_2}' \frac{T_{\ell_1\ell_1'L_1}^{0_1k_1} T_{\ell_2\ell_2'L_2}^{0_2k_2}}{\epsilon_{k_1} - \epsilon_{0_1} + \epsilon_{k_2} - \epsilon_{0_2}}.$$
(2.11)

contain contributions from dispersion and induction. The \sum' implies that $k_1 + k_2 \neq 0$ and ϵ_{k_i} is the energy of the k_i 'th state. The $\zeta_{L_1L_2M}^{\ell_1\ell'_1;\ell_2\ell'_2}$ coefficient is a scalar coupling term given by [75]

$$\zeta_{L_{1}L_{2}M}^{\ell_{0}\ell_{1}';\ell_{2}\ell_{2}'} = (-1)^{\ell_{2}+\ell_{2}'} ((2L_{1}+1)!(2L_{2}+1)!)^{1/2} \left[\frac{(2\ell_{1}+2\ell_{2}+1)!(2\ell_{1}'+2\ell_{2}'+1)!}{(2\ell_{1})!(2\ell_{1}')!(2\ell_{2})!(2\ell_{2}')!} \right]^{1/2} \\ \times \sum_{L} \eta_{L_{1}L_{2}L}^{M} (\ell_{1}+\ell_{2}0);\ell_{1}'+\ell_{2}'0|L0) \left\{ \begin{array}{cc} \ell_{1} & \ell_{1}' & L_{1} \\ \ell_{2} & \ell_{2}' & L_{2} \\ \ell_{1}+\ell_{2} & \ell_{1}'+\ell_{2}' & L \end{array} \right\}, \quad (2.12)$$

the symbol between curly brackets being a Wigner 9-j symbol [73], and the coupled transition moment for each monomer is defined as

$$T_{\ell_i \ell'_i L_i}^{0,k_i} = \sum_m \langle 0_i | Q_{\ell_i m} | k_i \rangle \langle k_i | Q_{\ell'_i - m} | 0_i \rangle (\ell_i m; \ell'_i - m | L_i 0)$$
(2.13)

where the indices k_i go over ground and excited states. These coupled transition moments also transform the same way as the electrostatic moments $\langle Q_{\ell m} \rangle$. It should be noted that from Eq.(2.11), contributions such as

$$T_{\ell_1\ell_1'L_1}^{0_10_1} \sum_{k_2 \neq 0} \frac{T_{\ell_2\ell_2'L_2}^{0_2k_2}}{\epsilon_{k_2} - \epsilon_{0_2}} + (1 \rightleftharpoons 2)$$
(2.14)

are associated with $(\mu_1)^2 \alpha_2 + (1 \rightleftharpoons 2)$ type induction terms. Contributions to Eq.(2.11) such as

$$\sum_{\substack{k_1 \neq 0\\k_2 \neq 0}} \frac{T_{\ell_1 \ell_1' L_1}^{0_1 k_1} T_{\ell_2 \ell_2' L_2}^{0_2 k_2}}{\epsilon_{k_1} - \epsilon_{0_1} + \epsilon_{k_2} - \epsilon_{0_2}}$$
(2.15)

are associated with $\alpha_1 \alpha_2$ type dispersion terms and can be related to a Casimir-Polder integral over imaginary frequencies of coupled dynamic polarizabilities.

It is convenient in practice to collect all terms with the same R-dependence in Eq.(2.10) into a single expression

$$V_{L_1L_2M}^{(k)}(R) = -\sum_n \frac{W_{nL_1L_2M}^{(k)}}{R^n}.$$
(2.16)

With the dispersion and induction contributions to Eq.(2.16) are calculated separately as

$$W_{nL_1L_2M}^{(2)} = W_{nL_1L_2M}^{(2,DIS)} + W_{nL_1L_2M}^{(2,IND)}.$$
(2.17)

The long range interaction then can be characterized by a van der Waals series of the form

$$E_{\text{int}}(R,\theta_1,\phi_1,\theta_2,\phi_2) = \sum_{nL_1L_2M} \frac{(W_{nL_1L_2M}^{(1)} - W_{nL_1L_2M}^{(2)})}{R^n} \times P_{L_1}^M(\cos(\theta_1))P_{L_2}^M(\cos(\theta_2))\cos(M(\phi_1 - \phi_2)).$$
(2.18)

2.2 Extension to general molecules

In section 2.1, the general theory of long range interactions between linear molecules was discussed. Given the generality of the expansion in Eq.(2.3) it is possible to extend the theory to the interactions between molecules with arbitrary symmetry. Given two arbitrary molecules at any given configuration the orientation of each individual molecule can be described by the Euler angles $\hat{r}_i = \omega_i = (\alpha_i, \beta_i, \gamma_i)$ with the relative position between the molecular center of mass defined as $\mathbf{R} = (R, \bar{\Omega}) = (R, \theta, \phi)$. Here θ_i is the projection angle of \hat{r}_i on \mathbf{R} , ϕ_i is the projection angle of \hat{r}_i on the x axis and (R, θ, ϕ) are the spherical vector components of \mathbf{R} . The most general expansion is then where the interaction energy is separated into a series of radial and angular basis functions

$$E_{\rm int}(\hat{r}_1, \hat{r}_2, \mathbf{R}) = \sum_{\{\Lambda\}} E_{\{\Lambda\}}(R) A_{\{\Lambda\}}(\omega_1, \omega_2, \bar{\Omega})$$
(2.19)

Here $\{\Lambda\} = (L_1, K_1, L_2, K_2, L)$ are the set of angular indices, $E_{\{\Lambda\}}(R)$ are purely radial functions for a rigid-rotor and $A_{\{\Lambda\}}(\omega_1, \omega_2, \bar{\Omega})$ is an angular basis the choice of which depends on the molecular symmetry (see Table 2.1 for an overview of the required terms for various molecular symmetries). For a molecule with arbitrary symmetry, the most general angular basis is compactly written as [74]

$$A_{\{\Lambda\}}(\omega_1,\omega_2,\bar{\Omega}) = \sum_{M_1,M_2,M} \begin{pmatrix} L_1 & L_2 & L \\ M_1 & M_2 & M \end{pmatrix} D_{M_1K_1}^{L_1}(\omega_1)^* D_{M_2K_2}^{L_2}(\omega_2)^* C_{LM}(\bar{\Omega}), \quad (2.20)$$

where

$$D_{M_iK_i}^{L_i}(\omega_i) = e^{-iM_i\alpha_a} d_{M_iK_i}^{L_i}(\beta_i) e^{-iL_i\gamma_a}$$

$$(2.21)$$

is a Wigner rotation matrix [76] and $C_{\ell m}(\hat{r}_i)$ is a Racah spherical harmonic [73, 77].

Molecular Symmetry		Principle	nciple $\{\Lambda\}$		· Indices		
Mon. 1	Mon. 2	Euler Angles					
Atom	Atom	$(0,0,0), (0,0,0), (heta,\phi)$	$L_1 = 0$	$K_1 = 0$	$L_2 = 0$	$K_2 = 0$	L
Atom	Linear	$(0,0,0), (\alpha_2,\beta_2,0), (\theta,\phi)$	$L_1 = 0$	$K_1 = 0$	L_2	$K_{2} = 0$	L
Linear	Linear	$(\alpha_1, \beta_1, 0), (\alpha_2, \beta_2, 0), (\theta, \phi)$	L_1	$K_1 = 0$	L_2	$K_{2} = 0$	L
Atom	General	$(0,0,0), (\alpha_2,\beta_2,\gamma_2), (\theta,\phi)$	$L_1 = 0$	$K_1 = 0$	L_2	K_2	L
Linear	General	$(\alpha_1, \beta_1, 0), (\alpha_2, \beta_2, \gamma_2), (\theta, \phi)$	L_1	$K_1 = 0$	L_2	K_2	L
General	General	$(\alpha_1, \beta_1, \gamma_1), (\alpha_2, \beta_2, \gamma_2), (\theta, \phi)$	L_1	K_1	L_2	K_2	L

Table 2.1. Principle Euler angles, $\omega_i = (\alpha_i, \beta_i, \gamma_i)$, and angular basis indices, $\{\Lambda\} = (L_1, K_1, L_2, K_2, L)$, for the angular dependence of the long range interaction, Eq.(2.19), involving various molecular symmetries.

The radial functions $E_{\{\Lambda\}}(R)$ can be evaluated using first- and second-order perturbation theory in the same way as shown in section 2.1 by expanding in terms of Eq.(2.6). The first-order electrostatic contribution of order L then is straight forwardly generalized from Eq.(2.8) to be

$$E_{\{\Lambda\}}^{(1)}(R) = \sum_{n} \delta_{L_1 + L_2 + 1, n} \frac{\tilde{W}_{n\{\Lambda\}}^{(1)}}{R^n}$$
(2.22)

$$\tilde{W}_{n\{\Lambda\}}^{(1)} = (-1)^{L_1} \delta_{L_1 + L_2, L} \left[\frac{(2L_1 + 2L_2 + 1)!}{(2L_1)!(2L_2)!} \right]^{1/2} \langle 0_1 | Q_{L_1 K_1} | 0_1 \rangle \langle 0_2 | Q_{L_2 K_2} | 0_2 \rangle \right]$$
(2.23)

To generalize Eq.(2.13) and Eq.(2.10) a few intermediate definitions are required to ensure a compact notation.

First we define the irreducible tensor product [73, 76, 77] between two sets of spherical tensors $\Gamma_{\ell m}$ and $\Gamma_{\ell'm'}$ to be

$$[\Gamma_{\ell m} \otimes \Gamma_{\ell' m'}]_M^L = \sum_{mm'} \Gamma_{\ell m} \Gamma_{\ell' m'}(\ell m; \ell' m' | LM).$$
(2.24)

The coupled transition moments in Eq.(2.13) can be then generalized by removing the coupling constraint that m = m' (or equivalently K = 0) to provide

$$\tilde{T}^{0_i k_i}_{\ell_i \ell'_i L_i K_i} = [\langle 0_i | Q_{\ell_i m_i} | k_i \rangle \otimes \langle k_i | Q_{\ell'_i m'_i} | 0_i \rangle]^{L_i}_{K_i}.$$

$$(2.25)$$

As the angular basis of Eq.(2.20) is in a L_1L_2L coupling scheme instead of the L_1L_2M coupling scheme of the linear molecule basis of Eq.(2.4), a new scalar coupling coefficient must be defined in the place of Eq.(2.12). This can be done by removing the L coupling term η and adjusting the normalization coefficients, providing

$$\tilde{\zeta}_{L_{1}L_{2}L}^{\ell_{0}\ell'_{1};\ell_{2}\ell'_{2}} = (-1)^{\ell_{2}+\ell'_{2}} ((2L_{1}+1)(2L_{2}+1)(2L+1))^{1/2} (\ell_{1}+\ell_{2}0;\ell'_{1}+\ell'_{2}0|L0) \\ \times \left[\frac{(2\ell_{1}+2\ell_{2}+1)!(2\ell'_{1}+2\ell'_{2}+1)!}{(2\ell_{1})!(2\ell'_{1})!(2\ell_{2})!(2\ell'_{2})!} \right]^{1/2} \begin{cases} \ell_{1} & \ell'_{1} & L_{1} \\ \ell_{2} & \ell'_{2} & L_{2} \\ \ell_{1}+\ell_{2} & \ell'_{1}+\ell'_{2} & L \end{cases} .$$
(2.26)

From these definitions the generalized form of Eq.(2.10) is compactly given as

$$E_{\{\Lambda\}}^{(2)} = -\sum_{\ell_0\ell_1'\ell_2\ell_2'} R^{-\ell_0-\ell_1'-\ell_2-\ell_2'-2} \tilde{\zeta}_{L_1L_2L}^{\ell_0\ell_1';\ell_2\ell_2'} \sum_{\substack{k_1k_2\\k_1+k_2\neq 0}} \frac{\tilde{T}_{\ell_1\ell_1'L_1K_1}^{00k_1}\tilde{T}_{\ell_2\ell_2'L_2K_2}^{00k_2}}{\epsilon_{k_1}-\epsilon_{0_1}+\epsilon_{k_2}-\epsilon_{0_2}}.$$
 (2.27)

This can be simplified analogous to Eq.(2.14) and Eq.(2.15) as

$$E_{\{\Lambda\}}^{(2)} = -\sum_{n} \frac{\tilde{W}_{n\{\Lambda\}}^{(2,DIS)} + \tilde{W}_{n\{\Lambda\}}^{(2,IND)}}{R^{n}}$$
(2.28)

$$\tilde{W}_{n\{\Lambda\}}^{(2,DIS)} = \sum_{\ell_1 \ell_1' \ell_2 \ell_2'} \delta_{\Sigma\{\ell\}+2,n} \tilde{\zeta}_{L_1 L_2 L}^{\ell_1 \ell_1'; \ell_2 \ell_2'} \sum_{k_1 \neq 0} \frac{T_{\ell_1 \ell_1' L_1 K_1}^{\nu_1 \kappa_1} T_{\ell_2 \ell_2' L_2 K_2}^{\nu_2 \kappa_2}}{\epsilon_{k_1} - \epsilon_{0_1} + \epsilon_{k_2} - \epsilon_{0_2}}$$
(2.29)

$$\tilde{W}_{n\{\Lambda\}}^{(2,IND)} = \sum_{\ell_1\ell'_1\ell_2\ell'_2} \delta_{\sum\{\ell\}+2,n} \tilde{\zeta}_{L_1L_2L}^{\ell_1\ell'_1;\ell_2\ell'_2} \left(\tilde{T}_{\ell_1\ell'_1L_1K_1}^{0,0_1} \sum_{k_2\neq 0} \frac{\tilde{T}_{\ell_2\ell'_2L_2K_2}^{0,2k_2}}{\epsilon_{k_2} - \epsilon_{0_2}} + (1 \rightleftharpoons 2) \right), \quad (2.30)$$

with $\{\ell\} = \{\ell_1, \ell'_1, \ell_2, \ell'_2\}$. The long range interaction between two arbitrary molecules can be written in terms of the now completely scalar $W^{(1,2)}_{n\{\Lambda\}}$ coefficients as

$$E_{\rm int}(\hat{r}_1, \hat{r}_2, \mathbf{R}) = \sum_{\{\Lambda\}} \sum_n R^{-n} \left(\tilde{W}_{n\{\Lambda\}}^{(1)} - \tilde{W}_{n\{\Lambda\}}^{(2,DIS)} - \tilde{W}_{n\{\Lambda\}}^{(2,IND)} \right) A_{\{\Lambda\}}(\omega_1, \omega_2, \bar{\Omega}).$$

It is convenient, when discussing molecular properties, to work with the uncoupled static multipole polarizability^{*}

$$\alpha_{\ell m \ell' m'} = 2 \sum_{k \neq 0} \frac{\langle 0|Q_{\ell m}|k\rangle \langle k|Q_{\ell' m'}|0\rangle}{\epsilon_k - \epsilon_0}.$$
(2.32)

The related dynamic uncoupled polarizability is given by

$$\alpha_{\ell m \ell' m'}(\omega) = 2 \sum_{k \neq 0} \frac{(\epsilon_k - \epsilon_0) \langle 0_i | Q_{\ell m} | k_i \rangle \langle k_i | Q_{\ell' - m'} | 0_i \rangle}{(\epsilon_k - \epsilon_0)^2 - \omega^2}.$$
(2.33)

Additionally the S(0) metric (e.g. Thomas-Reiche-Kuhn sum rule [78, 79]) [80] is defined in terms of the spherical transition moments as

$$S_k(0) = \frac{2}{3} \sum_{n \neq 0}^k (\epsilon_n - \epsilon_0) (|\langle 0|Q_{10}|k\rangle|^2 - \langle 0|Q_{11}|k\rangle\langle 0|Q_{1-1}|k\rangle.$$
(2.34)

2.2.1 Transformation of basis

The angular basis in Eq.(2.31) is called a L_1L_2L coupled basis. This leads to a more natural and compact angular basis for later use in molecular potentials. The linear case described in Section 2.1 and Eq.(2.18) is an expanded basis and is referred to as a L_1L_2M coupled basis. Using this other basis has the advantage of being

$$\alpha_{\ell\ell'LK} = \sum_{mm'} \alpha_{\ell m\ell'm'}(\ell m; \ell'm'|LK)$$

^{*}It should be noted that the coupled multipole polarizability is easily expressed after comparison to Eq.(2.24) as

more intuitive, as the coefficients decrease monotonically for increasing values of M. All results for linear molecules presented in this work are in the L_1L_2M basis for essentially historical reasons. As such it is convenient to give the basis projection needed to take the coefficients of linear molecules from Eq.(2.31) to Eq.(2.18):

$$W_{nL_1L_2M}^{(1,2)} = \sum_{L} (2L+1)^{-1/2} \eta_{L_1L_2L}^M \left[\tilde{W}_{n\{\Lambda\}}^{(1,2)} \right]_{\substack{K_1=0\\K_2=0}}.$$
(2.35)

Here $\eta_{L_1L_2L}^M$ is given by Eq.(2.5), and the linear molecule case is assumed $(K_1 = 0, K_2 = 0)$.

2.3 Rotational state dressing of long range interactions: general theory^{*}

The orientation and alignment[†] ($\langle \cos \theta \rangle$ and $\langle \cos^2 \theta \rangle$ respectively as illustrated in Fig. 2.1(a)) of polar molecules can be achieved through several mechanisms, the most direct of which is the coupling of rotational states by a polarizing external DC electric field, **F**. Increasing the strength, *F*, of the external electric field increases the number of rotational states coupled, thus tightening the orientation of the molecule in a cone of angle θ about the orientation of the field. To account for this rotational coupling adiabatically, we expand the dressed state rotational wave function of the (case a) molecule as a superposition of field-free symmetric top states

$$|\tilde{J}\tilde{M}\Omega\rangle = \sum_{J,M} a_{\{J\}} |JM\Omega\rangle, \qquad (2.36)$$

where the symmetric top states are given in term of Wigner rotation matrices $D^{J}_{-M-\Omega}(\omega)$ as [73]

$$|JM\Omega\rangle = (-1)^{M-\Omega} \left(\frac{2J+1}{8\pi^2}\right) D^J_{-M-\Omega}(\alpha,\beta,\gamma), \qquad (2.37)$$

where (α, β, γ) are the Euler angles of the molecule, and J the total angular momentum quantum number with projections M in the laboratory frame (LF) and Ω onto the molecular axis. The expansion coefficients $a_{\{J\}} = a_{M\Omega}^J$ dictate the levels of

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[†]The orientation and alignment of a dipole in an external field is given by the dipole-vector and field-vector correlation distribution. Expanding the distribution in terms of Legendre polynomials, the first odd term is $\cos \theta$ corresponding to the *orientation cosine* and the first even term is $\cos^2 \theta$ corresponding to the *alignment cosine*.

mixing between the different rotational states, and can be solved for by diagonalizing $\langle \tilde{J}' \tilde{M}' \Omega' | H | \tilde{J} \tilde{M} \Omega \rangle$. Here *H* is the symmetric top and dipole-field Hamiltonian

$$H = B(\mathbf{J}^2 + J_z^2) - \mathcal{D}F\cos\theta, \qquad (2.38)$$

where **J** is the angular momentum operator, J_z is the angular momentum projection on the z axis, B is the molecular rotational constant, \mathcal{D} is the dipole moment of the molecule, and θ is the angle between the external electric field of magnitude F and the molecular axis. The coefficients $a_M^J(F)$ then depend on the strength F of the field. While theoretically simple, this process can become experimentally challenging for molecules with small dipole moments or rotational constants, due to the large external fields required for strong alignment.

An alternative to simply increasing the static field magnitude is to add a separate polarizing laser field [81] that directly couples the rotational states of the molecule. However, to achieve both alignment and orientation control, time-dependent nonadiabatic effects are introduced into the dressed state wavefunction [66]. For the purposes of this work the investigation and inclusion of these nonadiabatic effects are unimportant as only the final dressed state is of interest. As such we present our alignment in terms of an applied external static field and, where practical, the number of strongly coupled rotational states.

The adiabatic dressed state basis for two molecules at large separation is given in terms of the product of each molecule dressed rotational wave functions

$$|\phi\rangle = |\tilde{J}_1 \tilde{M}_1 \Omega_1\rangle \otimes |\tilde{J}_2 \tilde{M}_2 \Omega_2\rangle.$$
(2.39)

The dressed state (DS) van der Waals interaction $E_{\text{int}}^{\text{DS}}(\mathbf{R})$ is calculated from the matrix elements of Eq.(2.19) in the dressed state basis,



Figure 2.1. (a) Schematic representation of an aligned diatomic molecule. Classically, the molecule precesses on a cone of angle θ about the electric field \mathbf{F} , with $\langle \cos \theta \rangle$ describing the average orientation of the molecule: with the dipole moment \mathcal{D} pointing towards \mathbf{F} for $\langle \cos \theta \rangle > 0$, and in the opposite direction for $\langle \cos \theta \rangle > 0$. The alignment, $\langle \cos^2 \theta \rangle$, describes the tightness of the rotational cone. (b) Lab-fixed frame molecular interaction geometry in the presence of an external field, where θ_F is the angle between the field and the vector \mathbf{R} joining the two molecules.

$$V_{\rm int}^{\rm DS}(\hat{r}_1, \hat{r}_2, \mathbf{R}) = \langle \phi | V_{\rm int}(\hat{r}_1, \hat{r}_2, \mathbf{R}) | \phi \rangle = \sum_{\{\Lambda\}} E_{\{\Lambda\}}(R) \langle \phi | A_{\{\Lambda\}}(\omega_1, \omega_2, \Omega) | \phi \rangle.$$
(2.40)

This expectation value can be reduced directly to a summation over radial long range coefficients and a LF angular function through the evaluation of a number of angular momentum coupling terms.

Starting from the observation that the expectation value of a Wigner rotation matrix with a symmetric top wave function has the simple value of

$$\langle J'M'\Omega'|D_{M_{L}K_{L}}^{L}(\omega)|JM\Omega\rangle = \int d^{3}r \sqrt{\frac{2J'+1}{8\pi}} D_{M'\Omega'}^{J'}(\omega) D_{M_{L}K_{L}}^{L}(\omega)(-1)^{M-\Omega} \sqrt{\frac{2J+1}{8\pi}} D_{-M-\Omega}^{J}(\omega) = (-1)^{M-\Omega} \left[(2J'+1)(2J+1) \right]^{1/2} \begin{pmatrix} J' & L & J \\ M' & M_{L} & M \end{pmatrix} \begin{pmatrix} J' & L & J \\ \Omega' & K_{L} & \Omega \end{pmatrix}.$$
(2.41)

Expanding the angular expectation value of $A_{\{\Lambda\}}(\omega_1, \omega_2, \Omega)$ as

$$\langle \phi | A_{\{\Lambda\}}(\omega_1, \omega_2, \Omega) | \phi \rangle = \sum_{M_1 M_2 M} \langle \tilde{J}_1' \tilde{M}_1' \Omega_1' | D_{M_1 K_1}^{L_1}(\omega_1) | \tilde{J}_1 \tilde{M}_1 \Omega_1 \rangle \\ \times \langle \tilde{J}_2' \tilde{M}_2' \Omega_2' | D_{M_2 K_2}^{L_2}(\omega_2) | \tilde{J}_2 \tilde{M}_2 \Omega_2 \rangle C_{LM}(\Omega), \quad (2.42)$$

we can immediately write down the solution of Eq.(2.40) by inserting Eq.(2.41) and (2.36) into (2.42) to obtain

$$\begin{aligned} V_{\rm int}^{\rm DS}(\hat{r}_1, \hat{r}_2, \mathbf{R}) &= \sum_{\{\Lambda\}} E_{\{\Lambda\}}(R) \sum_{M_{L_1}M_{L_2}M_L} C_{LM_L}(\bar{\Omega}) \\ \times \sum_{\substack{J_1M_1\Omega_1 \ J_2M_2\Omega_2 \\ J'_1M'_1\Omega'_1 \ J'_2M'_2\Omega'_2}} \sum_{(-1)^{M_1-\Omega_1}(-1)^{M_2-\Omega_2} \rho_{\{J_1\};\{J'_1\}} \rho_{\{J_2\};\{J'_2\}} \\ \times \left[(2J'_1+1)(2J_1+1)(2J'_2+1)(2J_2+1) \right]^{1/2} \begin{pmatrix} L_1 \ L \ L_2 \\ M_{L_1} \ M_L \ M_{L_2} \end{pmatrix} \\ \times \begin{pmatrix} J'_1 \ L_1 \ J_1 \\ M'_1 \ M_{L_1} \ M_1 \end{pmatrix} \begin{pmatrix} J'_2 \ L_2 \ J_2 \\ M'_2 \ M_{L_2} \ M_2 \end{pmatrix} \begin{pmatrix} J'_1 \ L_1 \ J_1 \\ \Omega'_1 \ K_{L_1} \ \Omega_1 \end{pmatrix} \begin{pmatrix} J'_2 \ L_2 \ J_2 \\ \Omega'_2 \ K_{L_2} \ \Omega_2 \end{pmatrix} \end{aligned}$$
(2.43)

or, after some rearrangement for computational ease,

$$V_{\text{int}}^{\text{DS}}(\hat{r}_1, \hat{r}_2, \mathbf{R}) = \sum_{LM_L} \sum_n \frac{C_{LM_L}(\bar{\Omega})\tilde{W}_{nLM_L}}{R^n}$$
(2.44)

with

$$\begin{split} \tilde{W}_{nLM_{L}} &= \sum_{\substack{L_{1}M_{L_{1}}K_{1} \\ L_{2}M_{L_{2}}K_{2} \\ J_{1}^{\prime}M_{1}^{\prime}\Omega_{1}^{\prime}J_{2}^{\prime}M_{2}^{\prime}\Omega_{2}^{\prime}}} \left[(2J_{1}^{\prime}+1)(2J_{1}+1)(2J_{2}^{\prime}+1)(2J_{2}+1) \right]^{1/2} \\ &\times (-1)^{M_{1}-\Omega_{1}+M_{2}-\Omega_{2}} \rho_{\{J_{1}\};\{J_{1}^{\prime}\}}\rho_{\{J_{2}\};\{J_{2}^{\prime}\}} \left(W_{n\{\Lambda\}}^{(1)} - W_{n\{\Lambda\}}^{(2)} \right) \begin{pmatrix} L_{1} & L & L_{2} \\ M_{L_{1}} & M_{L} & M_{L_{2}} \end{pmatrix} \\ &\times \begin{pmatrix} J_{1}^{\prime} & L_{1} & J_{1} \\ M_{1}^{\prime} & M_{L_{1}} & M_{1} \end{pmatrix} \begin{pmatrix} J_{2}^{\prime} & L_{2} & J_{2} \\ M_{2}^{\prime} & M_{L_{2}} & M_{2} \end{pmatrix} \begin{pmatrix} J_{1}^{\prime} & L_{1} & J_{1} \\ \Omega_{1}^{\prime} & K_{L_{1}} & \Omega_{1} \end{pmatrix} \begin{pmatrix} J_{2}^{\prime} & L_{2} & J_{2} \\ \Omega_{2}^{\prime} & K_{L_{2}} & \Omega_{2} \end{pmatrix} \end{aligned}$$

$$(2.45)$$

and where

$$\rho_{\{J_i\};\{J_i'\}} = a_{\{J_i\}}a_{\{J_i'\}} \tag{2.46}$$

is the rotational state density for molecule *i*. In addition to the transformation of the van der Waals interaction energy as given by Eq.(2.43), it is useful to have the dressed static moment, $\langle Q_{\ell m}^{DS} \rangle$, of a given molecule. For molecule *i*, this is readily obtained to be

$$\langle Q_{\ell m}^{DS} \rangle = \langle \tilde{J}'_i \tilde{M}'_i \Omega'_i | \langle Q_{\ell m} \rangle | \tilde{J}_i \tilde{M}_i \Omega_i \rangle = \sum_{\substack{J_i M_i \Omega_i \\ J'_i M'_i \Omega'_i}} \delta_{M_i, M'_i} (-1)^{M_i - \Omega_i} \rho_{\{J_i\}; \{J'_i\}}$$

$$\times \left[(2J_i + 1)(2J'_i + 1) \right]^{1/2} \begin{pmatrix} J'_i & \ell & J_i \\ M'_i & m & -M_i \end{pmatrix} \begin{pmatrix} J'_i & \ell & J_i \\ \Omega_i & m & -\Omega_i \end{pmatrix} \langle Q_{\ell m} \rangle.$$
(2.47)

2.4 Rotational state dressing of long range interactions: low DC field solution^{*}

In the low DC field limit, coupling between rotational states can be limited to just two states, allowing Eq.(2.38) to be solved analytically (note that $\Omega \equiv 0$ and M = 0). From this it is possible to obtain general expressions for the expectation value of the static and alignment moments as a function of the applied field. Transforming to the unitless field parameter $\xi = \xi_0 F$, with $\xi_0 = D/2B$, we obtain for the two state density

$$\rho_{JJ'} = \frac{1}{\sqrt{3}(3+4\xi^2+\sqrt{9+12\xi^2})} \begin{pmatrix} \frac{1}{2\sqrt{3}}(3+\sqrt{9+12\xi^2})^2 & \xi(3+\sqrt{9+12\xi^2})\\ \xi(3+\sqrt{9+12\xi^2}) & 2\sqrt{3}\xi^2 \end{pmatrix}.$$
(2.48)

Defining the low-field limit as $\xi \leq 1$, we can simplify[†] Eq.(2.48) by expanding each numerator and denominator in a power series about small ξ to second order to obtain

$$\rho_{JJ'} \simeq \frac{1}{3\sqrt{3}(1+\xi^2)} \begin{pmatrix} \sqrt{3}(3+2\xi^2) & \xi(3+\xi^2) \\ \xi(3+\xi^2) & \sqrt{3}\xi^2 \end{pmatrix} + \mathcal{O}(\xi^3),$$
(2.49)

while still preserving

$$Tr(\rho_{JJ'}) = 1.$$
 (2.50)

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[†]The validity of this approximation rests with the fact that only in the low field does the two state approximation hold. Higher fields necessarily couple higher J values and so break the two state approximation immediately.
With Eq.(2.49) the dressed state dipole and quadrupole moments are (computed from Eq.(2.47))

$$\langle Q_{10}^{\rm DS} \rangle(\xi) = \langle Q_{10} \rangle \frac{6\xi + 2\xi^3}{8(1+\xi^2)} ,$$
 (2.51)

and

$$\langle Q_{20}^{\rm DS} \rangle(\xi) = \langle Q_{20} \rangle \frac{2\xi^2}{15(1+\xi^2)} ,$$
 (2.52)

respectively, while the octopole moment has no two state contribution by symmetry. The orientation moment $\langle \cos \theta \rangle$ is given trivially by

$$\langle \cos \theta \rangle(\xi) = \langle Q_{10}^{\rm DS} \rangle(\xi) / \langle Q_{10} \rangle, \tag{2.53}$$

while alignment $\langle \cos^2 \theta \rangle$ can be calculated by noting that $\cos^2 \theta = \frac{1}{3}(1 + 2C_{1,0}(\theta))$ (where $C_{\ell,m}(\hat{r}_i)$ is a Racah spherical harmonic), providing the expression

$$\langle \cos^2 \theta \rangle(\xi) = \frac{15 + 19\xi^2}{45(1+\xi^2)}.$$
 (2.54)

So long as the number of coupled states is dominated by the first two states and $\xi \leq 1$, these approximate formula are accurate to a few percent. In Table 2.2 we have evaluated ξ_0 for all the heteronuclear alkali diatoms from the spectroscopic data in Table 3.6. It is also possible to evaluate Eq.(2.43) and (2.46) using the two state low-field approximation. Following the prescribed method discussed above, the low field-dressed-state van der Waals potential can be written to leading order as

$$E_{2\rm st}^{\rm DS}(\mathbf{R},\xi) \simeq \frac{\tilde{W}_{320}^{(1)}(\theta_F,\xi)}{R^3} + \frac{\tilde{W}_{540}^{(1)}(\theta_F,\xi)}{R^5} - \frac{W_{6000}^{(2)}}{R^6} - \frac{W_{8000}^{(2)}}{R^8}.$$
 (2.55)

	²³ Na	$^{39}\mathrm{K}$	$^{95}\mathrm{Rb}$	^{133}Cs
7 Li	0.0114	0.116	0.159	0.246
23 Na		0.253	0.413	0.684
$^{39}\mathrm{K}$			0.141	0.529
$^{95}\mathrm{Rb}$				0.635

Table 2.2. Tabulated values of the field strength coefficient $\xi_0 = D/2B$ for the heteronuclear alkali diatoms using the spectroscopic and electrostatic constants from Table 3.6. All units are in cm²/kV.

Here θ_F is the angle between the inter-molecular vector **R** and the field vector as illustrated in Fig. 2.1(b). The dipole-dipole and quadrupole-quadrupole contributions are (up to order ξ^5)

$$\tilde{W}_{320}^{(1)}(\theta_F,\xi) = \langle Q_{10} \rangle^2 \frac{3\sqrt{3}\xi + 6\xi^2 + 4\sqrt{3}\xi^3 + 4\xi^4}{27(1+\xi^2)^2} (1 - 3\cos^2\theta_F),$$

and

$$\tilde{W}_{540}^{(1)}(\theta_F,\xi) = \langle Q_{20} \rangle^2 \frac{\xi^4}{75(1+\xi^2)^2} (3-30\cos^2\theta_F + 35\cos^4\theta_F), \qquad (2.56)$$

respectively (note that there is no dipole-octopole contribution in the two state approximation) while $W_{n000}^{(2)}$ is the isotropic dispersion+induction coefficient. The anisotropic terms contribute less than a percent to the interaction energy and can be safely neglected.

Chapter 3

Anisotropic Long Range Molecular Interactions: Computation

3.1 Electronic structure calculations of the alkali diatoms^{*}

Transition moment calculations for use in the evaluation of Eq.(2.13) were done for the XX+XX and XY+XY combinations of alkali metal diatomic molecules with atoms from Li to Cs in the $X^{1}\Sigma_{g}^{+}$ ground state using a locally modified version of the GAMESS[82, 83] 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.(2.11) is taken in this work to be the total number of single excitations[†]. 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 [84] 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

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[†]This choice in excitation space is extremely versatile in cases where continuum contributions are negligible or where double excitations remain in the bound manifold.

	α_{300}	$\times 10^3$	0	$x_{331} \times 10$	3	0	$a_{332} \times 10^{-10}$	3	0	$a_{333} \times 10^{-10}$	3
Method	0-aug	1-aug	0-aug	1-aug	2-aug	0-aug	1-aug	2-aug	0-aug	1-aug	2-aug
CIS	347.8	362.5	106.7	251.1	321.5	63.0	190.4	248.1	6.7	56.1	146.9
TDHF	336.4	350.9	100.3	243.8	314.1	61.3	187.4	245.0	6.6	55.1	145.4
VWN	233.3	241.3	88.8	186.1	214.8	55.5	140.4	162.7	6.4	47.2	102.8
B3LYP	342.9	346.6	119.1	244.9	295.4	64.2	162.5	197.0	6.8	47.1	104.9
CB3LYP	277.8	281.4	99.4	206.1	245.0	57.0	145.8	172.9	6.3	44.8	100.6
B3PW91	324.1	337.1	124.0	242.8	283.6	69.5	162.9	194.3	7.1	52.7	105.5
PBE0	310.8	316.7	116.5	249.4	274.4	66.5	170.3	190.3	6.9	103.5	105.2
VFCI[2]		286.6			240.7			167.7			108.5

Table 3.1. Basis set convergence of the octopole static polarizability values for Na_2 evaluated using several *ab initio* and DFT methods.

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-28 [85] and ECP-46 [85] 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 the core-valence correlation energy [86] 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 uncoupled multipole polarizability defined by Eq.(2.32), which for linear molecules reduces to $\alpha_{\ell m\ell' m'} = \alpha_{\ell - m\ell' m'} \equiv \alpha_{\ell\ell' m}$. The octopole polarizability terms α_{300} are the most sensitive to the effects of higher angular momentum functions in the basis set, and were therefore used to asses 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.

System	Method	r_e (a.u.)	α_{\parallel} (a.u.)	α_{\perp} (a.u.)
Li_2	B3PW91	5.051	268.4	170.0
	PBE0	5.051	262.4	168.7
	VFCI*	5.051	305.2	162.4
	$VFCI^{\dagger}$	5.051	297.7	165.1
Na ₂	B3PW91	5.818	352.2	206.2
	PBE0	5.818	338.7	203.7
	VFCI*	5.818	378.5	162.4
	$VFCI^{\dagger}$	5.818	370.1	201.6
K_2	B3PW91	7.416	714.6	301.5
	PBE0	7.416	676.2	395.4
	VFCI*	7.416	708.2	359.6
	$VFCI^{\dagger}$	7.379	677.8	363.1
Rb_2	B3PW91	7.956	830.2	453.6
	PBE0	7.956	785.8	448.3
	$CCSD(T)/PolMe^{\ddagger}$	8.1225	916.1	445.4
	VFCI*	7.956	789.7	405.5
Cs_2	B3PW91	8.78	1096.0	577.8
	PBE0	8.78	1032.9	568.3
	VFCI*	8.78	1012.2	509.0

Table 3.2. Static dipole polarizability values for the $X^1\Sigma_g^+$ homonuclear alkali diatoms calculated at the experimental equilibrium bond length. Note that $\alpha_{\parallel} = \alpha_{1010}$ and $\alpha_{\perp} = \alpha_{111-1}$.

The effects of adding additional sets of diffuse even tempered spdf basis functions can be seen in Table 3.1. It was found that two additional sets of diffuse functions was necessary to achieve accurate results for our test case of Na₂. For a subset of the DFT functionals 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 spdf 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 W_6 van der Waals coefficients, are essentially converged using the unmodified def2 basis set. A similar procedure was recently used by Rappoport and Furche [87] to optimize the Karlsruhe def2 basis sets for molecular property calculations. 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 [85], 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.

System	Method	$\alpha_{110}{}^a$	α_{111}^{*}	$\bar{\alpha}^b$	α_{220}	α_{221}	α_{222}	$W_{6000}^{(2,\mathbf{DIS})}$	$W_{8000}^{(2,\mathbf{DIS})}$
LiNa	$PBE0^{c}$	300.0	185.5	223.7	9418.9	7035.6	3356.2	3.279[3]	4.982[5]
	VCI^d	347.6	181.8	237.0					
	CCSDT^{e}			237.8				$3.673[3]^{f}$	
LiK	$PBE0^{\ddagger}$	455.1	261.8	326.3	24164.4	15899.8	5939.6	5.982[3]	1.378[6]
	VCI§	489.7	236.2	320.7					
	CCSDT^{\P}			324.9				$6.269[3]^{\parallel}$	
LiRb	PBE0 [‡]	445.5	256.1	319.2	27815.3	18110.7	6359.2	6.193[3]	1.583[6]
	VCI§	524.3	246.5	339.1					
	CCSDT^{\P}			346.2				$6.323[3]^{\parallel}$	
LiCs	PBE0 [‡]	525.2	289.1	367.8	38723.9	24996.3	7935.8	7.700[3]	2.297[6]
	VCI§	597.0	262.5	374.0					
	CCSDT^{\P}			386.7				$7.712[3]^{\parallel}$	

27

Table 3.3. Multipole static polarizabilities, $\alpha_{\ell\ell' m}$, and isotropic van der Waals dispersion coefficients, $W_{n000}^{(2,\text{DIS})}$, up to order n = 8 of all the ground state LiX alkali diatoms through cesium evaluated at the equilibrium bond lengths r_e listed in Table 3.6. All values are presented in atomic units, and [n] denotes $\times 10^n$.

 $^c\mathrm{This}$ work.

 d Ref. [1].

 e Ref. [49].

^fRef. [49] evaluated using CCSD and the Tang-Slater-Kirkwood formula [90].

^{*a*}Note that the parallel and perpendicular static dipole polarizabilities, α_{\parallel} and α_{\perp} , correspond to $\ell \ell' m = 110$ and 111 respectively.

 $^{{}^{}b}\bar{\alpha} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$ is the average static dipole polarizability.

System	Method	$\alpha_{110}{}^a$	α_{111}^{*}	$\bar{\alpha}^b$	α_{220}	α_{221}	α_{222}	$W_{6000}^{(2,\mathbf{DIS})}$	$W_{8000}^{(2,\mathbf{DIS})}$
NaK	$PBE0^{\ddagger}$	472.7	280.6	344.6	16572.0	13035.0	6739.5	6.818[3]	1.268[6]
	VCI§	529.2	262.3	351.3					
	$\operatorname{CCSD}(\mathbf{T})^c$			363.8				$6.493[3]^d$	
NaPh	DBE0‡	504.6	285.2	258 /	25217.0	17771 7	7547 5	7 688[2]	1 700[6]
Marto	VCI§	504.0 572.0	280.3	300.4 377.5	20211.0	111111.1	1041.0	1.000[0]	1.750[0]
	VOI°	572.0	200.5	511.5					
NaCs	$PBE0^{\ddagger}$	587.3	323.2	411.2	37633.3	25245.7	9444.6	9.453[3]	2.641[6]
	VCI§	670.7	304.2	426.4					
KRb	$PBE0^{\ddagger}$	729.6	420.9	523.8	36974.1	27588.8	13100.9	1.349[4]	3.385[6]
	VCI§	748.7	382.9	504.8					
KCs	$PBE0^{\ddagger}$	836.7	468.6	591.3	56372.9	38791.7	16262.9	1.657[4]	5.038[6]
	VCI§	822.3	425.62	571.1					
DI G	DDD0 ⁺	001.0	F 0000	00 7 0	10005 0	0.04.04.0	10010 0	1 00 ([4]	F 100[6]
RbCs	PBE0 ⁺	901.0	502.0	635.0	48325.3	36401.8	18619.8	1.884[4]	5.188[6]
	VCI ³	904.0	492.3	602.8					

Table 3.4. Multipole static polarizabilities, $\alpha_{\ell\ell' m}$, and isotropic van der Waals dispersion coefficients, $W_{n000}^{(2,\text{DIS})}$, up to order n = 8 of all the ground state XY alkali diatoms through cesium evaluated at the equilibrium bond lengths r_e listed in Table 3.6. All values are presented in atomic units, and [n] denotes $\times 10^n$.

^aNote that the parallel and perpendicular static dipole polarizabilities, α_{\parallel} and α_{\perp} , correspond to $\ell \ell' m = 110$ and 111 respectively.

 ${}^{b}\bar{\alpha} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$ is the average static dipole polarizability.

 c Ref. [3].

^dRef. [3] evaluated using the London formula.

3.1.1 Choice of DFT functional

Using the double augmented basis set (d-aug-def2-QZVPP) described above two ab initio methods were considered for our test case Na₂, configuration interaction singles [91, 92] (CIS) and time dependent Hartree-Fock [92, 93] (TD-HF) theory. Additionally we used time dependent density functional theory (TD-DFT) [92, 93] to evaluate excitation energies and multipole transition moments. The results of the *ab initio* and TD-DFT calculations are compared to those of Spelsberg and Meyer [2] in Table 3.8. Despite the success [72] 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 [78, 79, 94], 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 [2] appears quite good. Upon examining the results of Table 3.8 we have chosen the B3PW91 and PBE0 functionals for use in the rest of this work due to their consistent accuracy for both dispersion and induction interactions.

3.2 Numerical Results

3.2.1 Electrostatic Moments

The leading order term of the long range expansion Eq.(2.18), and thus the longest ranged interaction in the series, involve products of the electrostatic moments of each monomer, and for dipolar molecules, it is the dipole-dipole R^{-3} term. The dipole-dipole scattering [95] and applications of dipole-dipole interactions [58] are well studied in the literature, however higher order terms can be necessary for accurately describing intermediate intermolecular distances [5], and are often neglected if only

$n L_1 L_2 M$	Li_2	Na ₂	K_2	Rb_2	Cs_2
Q_{20}	10.74	10.52	15.68	16.06	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 3.5. Electrostatic van der Waals coefficients, $W_{nL_1L_2M}^{(1)}$, for the ground state alkali dimers Li₂, Na₂, K₂, Rb₂ and Cs₂ calculated at the CCSD(T) level of theory using the finite field method. All values are reported in atomic units and (n) denotes $\times 10^n$.

for a lack of available data. As such, we have calculated the *ab initio* electrostatic dipole, quadrupole and octopole moments (higher order moments do not contribute up to R^{-5} in the long range expansion. The electrostatic moments were calculated using coupled cluster theory including all singles, doubles and perturbative triples (CCSD(T)) [96, 97], using a two step finite field method (with field spacings of 10^{-6} a.u.). The inner valence *s* and *p* electrons were included in the correlation treatment to account for core-core and core-valence contributions. For consistency the n-def2-QZVPP basis sets defined above were used. Comparisons with the results of Harrison and Lawson [98] for Li₂, Na₂ and K₂ show that this choice of basis set provides reliable results.

In Table 3.5 we show our calculated quadrupole moment and R^{-5} van der Waals coefficients for the homonuclear alkali diatoms including new results for Rb₂ and Cs₂. Table 3.6 shows our calculated static moments, the outer turning point R_q for each system^{*}, as well as various dipole and quadrupole moments found in the literature for the heteronuclear alkali diatoms. Our computed static dipole moments agree closely

*

 $E_{\rm int}(R_q, 0, 0, 0) = -\frac{\langle Q_{10} \rangle^2}{R_q^3} + \frac{3\langle Q_{20} \rangle^2 - 4\langle Q_{10} \rangle \langle Q_{30} \rangle}{R_q^5} = 0.$ (3.1)

with both the valence full configuration interaction results of Aymar *et al.* [99] and González-Férez *et al.* [100] across all the molecules investigated, and the CCSDT (CCSD with all triples) results of Quéméner *et al.* [49] for the highly polar LiX (X=Na,K,Rb,Cs) species. Other than the CCSD(T) quadrupole moment of Zemke *et al.* [3] (with which we compare well), little to no published quadrupole values exist for the heteronuclear alkali diatoms. It has been demonstrated for the homonuclear alkali diatoms that the finite field CCSD(T) higher order static moments compare well with other methods [5, 98]; similar accuracy is anticipated for the heteronuclear species.

System	Method	r_e^*	$\langle Q_{10} \rangle$	$\langle Q_{20} \rangle$	$\langle Q_{30} \rangle$	R_q
LiNa	$CCSD(T)^*$	5.45	0.20	10.07	-47.33	95
	VCI^{\dagger}	5.43	0.22			
	$\mathrm{CCSDT}^{\ddagger}$	5.45	0.21			
LiK	$CCSD(T)^{\dagger}$	6.27	1.39	6.07	-59.99	15
	VCI [‡]	6.21	1.39			
	$\mathrm{CCSDT}^{\$}$	6.27	1.38			
1.151			1 00	a - a	00.44	10
LiRb	$\operatorname{CCSD}(T)'$	6.50	1.63	2.76	-62.41	13
	VCI ⁺	6.48	1.63			
	CCSD ₁ 3	6.50	1.59			
T:Ca	$CCCD(T)^{\dagger}$	6 02	9.15	2.20	10 99	10
LIUS	VCI [‡]	0.95	$2.10 \\ 0.17$	-2.29	-49.00	10
	VCI* CCSDT§	0.82	2.17 9.11			
	CC3D1.	0.95	2.11			
NaK	$CCSD(T)^{\dagger}$	6 61	1 12	10.56	-26 54	19
1,0011	$CCSD(T)^{\S}$	6 592	1 156	10.60	20.01	10
	VCI [‡]	6.49	1.100	10.00		
	VOI	0.10	1.00			
NaRb	$CCSD(T)^{\dagger}$	6.88	1.35	6.94	-56.00	16
	VCI [‡]	6.84	1.30			-
NaCs	$CCSD(T)^{\dagger}$	7.27	1.85	2.49	-60.45	12
	VCI [‡]	7.20	1.83			
KRb	$CCSD(T)^{\dagger}$	7.69	0.25	15.14	-69.09	109
	VCI^{\ddagger}	7.64	0.23			
	rel^{\P}	7.7	0.30			
KCs	$\operatorname{CCSD}(\mathrm{T})^{\dagger}$	8.10	0.75	13.00	-105.70	38
	VCI [‡]	8.02	0.76			
		0.07	0.40	15 00	50.00	00
RbCs	$CCSD(T)^{\dagger}$	8.37	0.49	15.88	-50.28	60
	VCI ⁺	8.30	0.40			

Table 3.6. Center of mass multipole electrostatic moments, $\langle Q_{\ell 0} \rangle$ ($\ell = 1, 2, 3$ corresponds to dipole, quadrupole and octopole moments respectively), of all the ground state heteronuclear alkali diatoms through cesium evaluated at the equilibrium bond length r_e (r_e values are taken from experimental results where available, see Deiglmayr *et al.* [1] and references therein). The variable R_q denotes the distance where the R^{-5} electrostatic term overcomes the dipole-dipole R^{-3} contribution. All values are presented in atomic units.



Figure 3.1. Diatom-diatom coordinate system.

3.2.2 Homonuclear alkali diatomics^{*}

Isotropic dispersion interactions between Na₂ and K₂ pairs have been previously studied using the London formula [3] and time dependent density functional theory (TD-DFT) [102, 103]. Spelsberg *et al.* [2] have calculated van der Waals coefficients including anisotropic corrections using valence full configuration interaction (VFCI) theory for Li₂, Na₂ and K₂. Also recent work by Kotochigova [104] has calculated the isotropic van der Waals interaction for KRb with leading order anisotropic corrections. In this work 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. Extensions to heteronuclear alkali diatomic van der Waals interactions and to larger alkali clusters will be presented in Section 3.2.3

As the leading dispersion interaction term W_6 is proportional to the product of the dipole polarizabilities, and the higher-order terms are proportional to products of the

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quadrupole and higher polarizabilities, the multipole polarizabilities required at each order must be accurately calculated. 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 3.2 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 [105]. Because the polarizability is very sensitive to the diatomic bond distance near equilibrium [88], 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 (α_{111}) agrees better with the existing theoretical results than the parallel polarizability (α_{110}). For the higher order polarizabilities, the only available values come from Spelsberg et al. [2]. 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.

As noted previously, the Karlsruhe def2 basis sets replace the inner core^{*} electrons of rubidium and cesium with an effective core potential. In order to assess the effect of the ECP on the calculated dispersion coefficients, we have performed all-electron calculations on Rb_2 using the Urban and Sadlej optimized triple zeta PolMe basis set [106] and the Douglas-Kroll-Hess Hamiltonian [107, 108]. Comparison with ECP calculations using the valence functions from the PolMe basis show that the inner

^{*}In this work, inner core refers to the Ne core for Rb and the Ar core for Cs.



Figure 3.2. comparison of the van der waals surface of collinear na_2 with both the london isotropic v_6 approximation [3] and a fully *ab initio* curve.

INA4
(4)
(4)
$1.532(4)^*$
$(4)^{\ddagger} 1.817(4)^{\dagger}$
(4)
(4)

Table 3.7. Comparison of theoretical isotropic W_6 van der Waals coefficients. All values are reported in atomic units and (n) denotes $\times 10^n$.

core contribution increases the calculated value of W_6 by 6%. We expect a similar or slightly greater effect for Cs₂.

Often neglected, the leading order term in the van der Waals expansion for homonuclear alkali diatoms is the electrostatic W_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 ~ 13cm⁻¹ for the co-linear orientation ($\theta_1 = \theta_2 = 0$, see Figure 3.1). 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.* [3] as well as for the related systems of K_2+Rb_2 [10] and Rb_2+Cs_2 [109] where the lowest energy reaction path was calculated *ab initio* and indeed was found to be barrierless. To illustrate the effect of including the W_5 electrostatic term as well as the higher order W_8 terms, the results of the London approximation given by Zemke *et al.* [3] are compared in Fig. 3.2 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 [110, 111]. As can be seen in Fig. 3.2, the inclusion of W_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 W_5 van der Waals coefficient evaluates to zero. For this case the leading order term in the van der Waals series is the isotropic W_6 dispersion interaction (the isotropic contribution is found by evaluating Eq.(2.7) for $L_1 = L_2 = M = 0$). We compare our calculated W_6 coefficients to existing theoretical results in Table 3.7. For the case of Li₂ it can be seen that B3PW91 performs well, which is also true from Table 3.8 for the case of Na₂. For the heavier K₂ we find that PBE0 performs marginally better for W_6 . In Table 3.9 all the calculated van der Waals coefficients including all anisotropic contributions for Li₂ and K₂ are presented. To compare with the results of Spelsberg *et al.* [2] 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

$$W_{L_1L_2M} = \sum_L \eta^M_{L_1L_2L} V_{L_1L_2L}.$$
(3.2)

After recoupling, we find our van der Waals coefficients to be in good agreement with those of Spelsberg *et al.*. Also in Table 3.9 are our new results for Rb_2 and Cs_2 . Using the aug-def2-QZVPP basis set and ECP, our calculations for Rb_2 and Cs_2 contain comparable numbers of electrons to the all-electron calculations for Na_2 , and therefore we expect our van der Waals coefficients for these alkali diatoms to be comparably accurate.

$n L_1 L_2 M$	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(3)	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)	-5.251(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)
$\% \mathrm{RMS}$	44.6	5.8	2.8	5.5	6.1	1.4	2.3
Dispersion							
$8 \ 0 \ 0 \ 0$	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)	-9.951(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)
Induction							
$8\ 0\ 0\ 0$	1.401(5)	1.086(5)	1.073(5)	4.984(4)	6.712(4)	7.579(4)	7.459(4)
$8\ 2\ 0\ 0$	9.006(4)	6.887(4)	6.834(4)	3.237(4)	4.335(4)	4.909(4)	4.802(4)
$8\ 2\ 2\ 0$	3.576(4)	2.425(4)	2.511(4)	1.390(4)	1.784(4)	2.067(4)	1.928(4)
$8\ 2\ 2\ 1$	-7.153(3)	-4.849(3)	-5.022(3)	-2.779(3)	-3.569(3)	-4.134(3)	-3.855(3)
$8\ 2\ 2\ 2$	1.788(3)	1.212(3)	1.256(3)	6.948(2)	8.922(2)	1.033(3)	9.639(2)
$8\ 4\ 0\ 0$	6.003(4)	4.656(4)	4.598(4)	2.136(4)	2.877(4)	3.248(4)	3.197(4)
$8\ 4\ 2\ 0$	4.721(4)	3.201(4)	3.315(4)	1.834(4)	2.355(4)	2.728(4)	2.545(4)
$8\ 4\ 2\ 1$	-6.438(3)	-4.364(3)	-4.520(3)	-2.501(3)	-3.212(3)	-3.720(3)	-3.470(3)
$8\ 4\ 2\ 2$	3.576(2)	2.425(2)	2.511(2)	1.390(2)	1.784(2)	2.067(2)	1.928(2)
%RMS	22.1	7.3	8.0	5.5	8.6	3.0	4.3

Table 3.8. Unique calculated dispersion and induction van der Waals coefficients, $W_{nL_1L_2M}^{(2)}$, for ground state Na₂ using selected *ab initio* and DFT methods. The RMS deviations are relative to previous theoretical results [2]. All calculations are performed at the experimental equilibrium bond length, values are reported in atomic units and (n) denotes $\times 10^n$.

	L	i ₂	k	X_2	R	b_2	С	S ₂
$n L_1 L_2 M$	B3PW91	- PBE0	B3PW91	PBE0	B3PW91	PBE0	B3PW91	PBE0
Dispersion								
6000	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)
$\% \mathrm{RMS}$	2.7	3.4	8.8	6.4				
Dispersion								
$8\ 0\ 0\ 0$	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)	4.333(5)	8.191(5)	6.897(5)	1.788(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)
Induction								
$8 \ 0 \ 0 \ 0$	6.032(4)	3.075(5)	3.447(5)	3.390(5)	4.223(5)	4.199(5)	6.083(5)	6.174(5)
$8\ 2\ 0\ 0$	3.837(4)	1.236(5)	2.254(5)	2.196(5)	2.779(5)	2.736(5)	4.036(5)	4.057(5)
$8\ 2\ 2\ 0$	1.393(4)	2.717(4)	1.016(5)	9.269(4)	1.308(5)	1.203(5)	2.000(5)	1.889(5)
$8\ 2\ 2\ 1$	-2.787(3)	-3.771(3)	-2.032(4)	-1.854(4)	-2.615(4)	-2.407(4)	-4.000(4)	-3.778(4)
$8\ 2\ 2\ 2$	6.967(2)	1.629(2)	5.080(3)	4.634(3)	6.538(3)	6.016(3)	1.000(4)	9.445(3)
$8\ 4\ 0\ 0$	2.585(4)	1.698(3)	1.477(5)	1.453(5)	1.810(5)	1.800(5)	2.607(5)	2.646(5)
$8\ 4\ 2\ 0$	1.839(4)	1.284(3)	1.341(5)	1.224(5)	1.726(5)	1.588(5)	2.640(5)	2.494(5)
$8\ 4\ 2\ 1$	-2.508(3)	-1.680(2)	-1.829(4)	-1.668(4)	-2.354(4)	-2.166(4)	-3.600(4)	-3.400(4)
$8\ 4\ 2\ 2$	1.393(2)	8.254(0)	1.016(3)	9.269(2)	1.308(3)	1.203(3)	2.000(3)	1.889(3)
%RMS	4.5	5.4	7.2	5.9				

Table 3.9. Unique van der Waals coefficients, $W_{nL_1L_2M}^{(2)}$, for the ground state alkali dimers Li₂, K₂ and new results for Rb₂ and Cs₂ calculated at the TD-DFT level of theory using the B3PW91 and PBE0 functionals. The RMS deviations are relative to previous theoretical results [2] where applicable. All calculations are performed at the experimental equilibrium bond length, values are reported in atomic units and (n) denotes $\times 10^n$.

3.2.3 Heteronuclear alkali diatomics^{*}

In this section we present our computational results on the heteronuclear alkali diatoms from LiNa to RbCs. Several papers have discussed the isotropic R^{-6} interactions of homonuclear alkali diatoms using both the London approximation [3] and time dependent density functional theory (TD-DFT) [102, 103]. The isotropic and anisotropic contributions have been investigated using configuration interaction [2] and TD-DFT [5] to compute van der Waals coefficients through R^{-8} . However, systematic research on the heteronuclear alkali diatoms is limited to the R^{-6} isotropic van der Waals coefficients for the LiX (X=Na,K,Rb,Cs) species [49]. Prior to our work, the only heteronuclear anisotropic van der Waals coefficients available in the literature are for KRb and RbCs [104] and limited to R^{-6} dispersion forces. We performed a systematic study of the isotropic and anisotropic van der Waals interactions through order R^{-8} of the heteronuclear alkali [6] rigid-rotor diatoms in their absolute ground state as a continuation of our work on the homonuclear species [5].

Dispersion and induction contributions to the van der Waals series are proportional to different products of the dipole, quadrupole and octopole polarizabilities. As such we have calculated and presented in Tables 3.3 and 3.4 the dipole and quadrupole static polarizabilities with comparisons to some of the existing literature (octopole static polarizabilities are not listed, but are available upon request). As discussed previously [5], the n-aug-def2-QZVPP basis sets are well converged for computation of static polarizabilities of homonuclear alkali diatoms up to octopole order, and we find the same is true for the heteronuclear species. Density functional methods are known to provide average static polarizabilities to within five to ten percent of experimental or highly correlated results [112, 113]. Furthermore some variance is expected

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in the parallel (α_{110}) polarizability as all computations are done at the experimental (or theoretical where necessary) equilibrium bond length, and it is well known that the polarizability is sensitive to the internuclear separation in the alkali diatoms [1]. It is expected that the perpendicular polarizability (α_{111}) should agree much more closely with other methods, which we find to be the case as illustrated in Tables 3.3 and 3.4.

Van der Waals dispersion and induction coefficients of the heteronuclear alkali diatoms are sparsely given in the literature. Currently only a few values exist and are restricted to isotropic contributions (corresponding to $W_{6000}^{2,\text{DIS}}$). The only systematic calculations are for the LiX species [49]. In Tables 3.3 and 3.4 we note the reasonable agreement between our reported TD-DFT isotropic $C_6 = W_{6000}^{2,\text{DIS}}$ dispersion coefficients and the Tang-Slater-Kirkwood [90] values from Quéméner et al. [49] for the LiX species. Additionally Kotochigova [104] has calculated, using multireference configuration interaction theory, the isotropic and anisotropic dispersion coefficients of order R^{-6} for both KRb and RbCs. However, these values contain non-Born-Oppenheimer contributions and so are not directly comparable to our numbers; because of this we have not included these values in Tables 3.3 and 3.4. To determine the accuracy of the van der Waals coefficients calculated here, we have computed ab*initio* curves for LiNa+LiNa at two different molecular frame geometries using the CCSD(T)-F12a/QZVPP (explicitly correlated CCSD(T)) level of theory [110, 111]. These *ab initio* curves are plotted in Fig. 3.3 along with the electrostatic plus isotropic dispersion approximation and the the van der Waals curves of this work including all anisotropic terms through R^{-8} . As can be seen, the TD-DFT van der Waals curves agree to a few cm^{-1} with the *ab initio* results , while the isotropic curves fail completely in the intermediate-range (it should be noted that for the collinear case of LiNa+LiNa the isotropic curves do not turn over at all and predict an infinite repul-



Figure 3.3. Plotted is a comparison of interaction curves at various orientations for molecule-fixed-frame LiNa+LiNa (in the absence of an external electric field) at different levels of theory. The black open circles is a fully *ab initio* curve computed at the CCSD(T)-f12a/QZVPP level of theory (see text for computational details), the solid red line is the evaluation of the van der Waals expansion of Eq.(2.18) using TD-DFT to compute the dispersion coefficients (see Tables 3.10 and 3.11) and the dashed red line is the usual isotropic approximation containing angular dependent electrostatic terms where the dispersion contribution is truncated at the isotropic C_6 coefficient.

sive wall). In fact, even at the highly correlated level of theory used in computing the *ab initio* curves in Fig. 3.3, there is a several cm^{-1} difference in barrier heights between the CCSD(T)-F12a and CCSD(T)-F12b explicitly correlated methods demonstrating the difficulty in obtaining reliable results for molecular interaction barriers at long range. In Tables 3.10 and 3.11 we have listed the $W_{nL_1L_2M}^{(1,2)}$ coefficients for all of the heteronuclear alkali diatoms, including all terms up through order R^{-8} .

$n L_1 L_2 M$	LiNa	LiK	LiRb	LiCs
Electrostatic	$: W_{nL_1L_2M}^{(1)}$			
3110	-7.076[0]	-3.799[0]	-5.170[0]	-9.094[0]
3111	0.038[0]	1.900[0]	2.585[0]	4.547[0]
4210	-5.893[0]	-2.547[1]	-1.431[1]	1.324[1]
4211	1.965[0]	8.489[0]	4.771[0]	-4.412[0]
5220	6.086[2]	2.276[2]	5.284[1]	2.568[1]
5221	-1.353[2]	-5.058[1]	-1.174[1]	-5.707[0]
5222	8.453[0]	3.161[0]	0.734[0]	0.357[0]
5310	3.674[1]	3.306[2]	2.887[2]	3.942[2]
5311	-9.186[0]	-8.266[1]	-7.218[1]	-9.855[1]
Dispersion+	Induction:	$W^{(2)}_{nL_1L_2M}$		
6000	3.289[3]	7.243[3]	7.254[3]	1.062[4]
6200	4.036[2]	3.479[2]	4.874[2]	2.739[1]
6220	1.768[2]	1.180[3]	1.094[3]	2.567[3]
6221	-3.929[1]	-2.621[2]	-2.430[2]	-5.705[2]
6222	4.911[0]	3.277[1]	3.038[1]	7.131[1]
7100	1.075[3]	-4.898[2]	-5.906[3]	-3.740[4]
7210	1.460[2]	-7.641[3]	-8.641[3]	-3.110[4]
7211	-2.433[1]	1.273[3]	1.440[3]	5.184[3]
7300	7.411[2]	4.567[3]	1.057[3]	-9.020[3]
7320	4.259[2]	-7.013[2]	-2.682[3]	-1.687[4]
7321	-7.099[1]	1.169[2]	4.470[2]	2.812[3]
7322	5.070[0]	-8.349[0]	-3.193[1]	-2.008[2]
8000	5.586[5]	1.539[6]	1.715[6]	2.722[6]
8200	3.552[5]	1.270[6]	1.534[6]	2.793[6]
8220	9.460[4]	5.702[5]	6.695[5]	1.636[6]
8221	-1.406[4]	-8.078[4]	-9.379[4]	-2.272[5]
8222	1.234[3]	4.607[3]	4.642[3]	9.978[3]
8400	3.896[4]	4.574[4]	6.320[4]	1.371[5]
8420	2.706[4]	7.284[4]	8.377[4]	2.485[5]
8421	-3.666[3]	-9.822[3]	-1.124[4]	-3.320[4]
8422	2.001[2]	5.287[2]	5.965[2]	1.740[3]

Table 3.10. LiX (X=Na,K,Rb,Cs) calculated CCSD(T) electrostatic and TD-DFT dispersion+induction van der Waals coefficients, $W_{nL_1L_2M}^{(1,2)}$, for unique combinations of L_1L_2M . All values are presented in atomic units and calculated at the equilibrium bond length r_e listed in Table 3.6, and [n] denotes $\times 10^n$.

$n L_1 L_2 M$	NaK	NaRb	NaCs	KRb	KCs	RbCs
Electrostatio	$W_{nL_{1}L_{2}M}^{(1)}$					
3110	-2.470[0]	-3.651[0]	-6.813[0]	-0.125[0]	-1.164[0]	-0.432[0]
3111	1.235[0]	1.826[0]	3.406[0]	0.063[0]	0.582[0]	0.216[0]
4210	-3.528[1]	-2.818[1]	-1.377[1]	-1.134[1]	-2.960[1]	-2.221[1]
4211	1.176[1]	9.393[0]	4.590[0]	3.785[0]	9.867[0]	7.403[0]
5220	6.717[2]	2.900[2]	3.710[1]	1.375[3]	1.004[3]	1.524[3]
5221	-1.493[2]	-6.444[1]	-8.245[0]	-3.056[2]	-2.231[2]	-3.386[2]
5222	9.329[0]	4.028[0]	0.515[0]	1.910[1]	1.395[1]	2.116[1]
5310	1.175[2]	7.346[1]	5.962[1]	6.909[1]	1.955[2]	1.106[1]
5311	-2.937[1]	-1.836[1]	-1.490[1]	-1.727[1]	-4.887[1]	-2.764[0]
Dispersion+	Induction:	$W^{(2)}_{nL_1L_2M}$				
6000	7.777[3]	8.680[3]	1.233[4]	1.354[4]	1.726[4]	1.921[4]
6200	5.519[2]	7.837[2]	3.327[2]	2.001[3]	2.375[3]	2.909[3]
6220	9.762[2]	1.223[3]	2.694[3]	1.028[3]	1.826[3]	1.857[3]
6221	-2.169[2]	-2.717[2]	-5.986[2]	-2.284[2]	-4.059[2]	-4.127[2]
6222	2.712[1]	3.397[1]	7.482[1]	2.855[1]	5.073[1]	5.159[1]
7100	1.157[4]	2.268[3]	-2.114[4]	6.069[3]	1.457[4]	1.755[4]
7210	-1.657[1]	-4.434[3]	-2.312[4]	9.929[2]	-8.871[2]	2.795[3]
7211	2.762[0]	7.391[2]	3.853[3]	-1.655[2]	1.479[2]	-4.658[2]
7300	9.136[3]	4.795[3]	-1.280[3]	4.176[3]	1.234[4]	1.231[4]
7320	4.931[3]	1.142[3]	-9.091[3]	2.772[3]	7.134[3]	8.669[3]
7321	-8.219[2]	-1.903[2]	1.515[3]	-4.621[2]	-1.189[3]	-1.445[3]
7322	5.870[1]	1.360[1]	-1.082[2]	3.300[1]	8.492[1]	1.032[2]
8000	1.444[6]	1.928[6]	3.016[6]	3.734[6]	5.391[6]	5.667[6]
8200	8.920[5]	1.503[6]	2.766[6]	2.606[6]	4.295[6]	3.923[6]
8220	3.296[5]	6.003[5]	1.466[6]	7.941[5]	1.494[6]	1.296[6]
8221	-4.768[4]	-8.470[4]	-2.042[5]	-1.162[5]	-2.138[5]	-1.878[5]
8222	3.368[3]	4.596[3]	9.349[3]	9.098[3]	1.356[4]	1.351[4]
8400	6.476[4]	6.275[4]	1.107[5]	2.931[5]	3.258[5]	4.238[5]
8420	5.979[4]	7.214[4]	1.962[5]	2.200[5]	2.678[5]	3.389[5]
8421	-8.081[3]	-9.702[3]	-2.625[4]	-2.970[4]	-3.612[4]	-4.566[4]
8422	4.380[2]	5.183[2]	1.380[3]	1.603[3]	1.945[3]	2.453[3]

Table 3.11. XY (X,Y=Na,K,Rb,Cs) calculated CCSD(T) electrostatic and TD-DFT dispersion+induction van der Waals coefficients, $W_{nL_1L_2M}^{(1,2)}$, for unique combinations of L_1L_2M . All values are presented in atomic units and calculated at the equilibrium bond length r_e listed in Table 3.6, and [n] denotes $\times 10^n$.

Chapter 4 Molecular Rotational State Control

4.1 Controllable binding of polar molecules and meta-stability of 1-D gases with attractive dipole forces^{*}

The recent achievements in the formation and manipulation of ultracold polar molecules [38, 42] have opened the gate to exciting new studies in several fields of physical sciences. Polar molecules could find uses in quantum information [56] and precision measurements [44], while their long range and anisotropic interactions in dense samples could provide a fertile ground for novel quantum gases [53]. In addition, advances in controlling the alignment and orientation of polar molecules [65, 66] enable the manipulation of these inter-molecular interactions, building a bridge between atomic, molecular, and optical (AMO) physics, physical chemistry, and condensed matter physics. Until now, stable dipolar gases were thought to require a repulsive dipole-dipole interaction, such as provided by parallel dipoles perpendicular to a 2-D plane. However, to observe interesting new correlations and phases, such as the Luttinger liquid transition [54] attractive interactions are needed. In this work, a system with such features is proposed and investigated, which combines available techniques to produce ultracold polar molecules with the ability to precisely control their orientation.

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In this section, we focus on KRb, which has been trapped in relatively large amounts [38]. We first calculate the potential energy surface (PES) $V(R, \theta_1, \theta_2, \phi)$ of two KRb molecules approaching each other for a wide range of geometries. We assume that both molecules are in the ro-vibrational ground state of their electronic ${\rm X}^{1}\Sigma^{+}$ ground state, and rigid rotors, an approximation that is valid for $R\sim 20$ a.u. or larger. Fig. 4.1 shows the PES for three particular geometries when both molecular axes are in the same plane ($\phi = 0$): the top, middle and bottom panels depict V when the molecules are aligned $(\theta_1 = \theta_2 = 90^\circ)$, in the *T*-orientation $(\theta_1 = 0, \theta_2 = 90^\circ)$, and collinear ($\theta_1 = \theta_2 = 0$) respectively. Those curves illustrate the difference between the stronger short-range region where the electronic wavefunction becomes perturbed and the weaker long range region where the bond length of each KRb is not affected. The short-range region is generally deep and strongly angular dependent, with wells ranging from a few 100 K in Fig. 4.1 for co-planar geometries, to the tetramer K_2Rb_2 bound by ~ 4300 K with respect to the KRb+KRb threshold [10, 11]. The KRb+KRb PES was calculated at the CCSD(T) level of theory using MOLPRO 2009.1 [114, 115], with the K and Rb core electrons replaced by the Stuttgart relativistic ECP18SDF [116] and ECP36SDF [117] pseudopotentials, respectively. The core-valence correlation energy was modeled using a core polarization potential [116]. Supplemental basis functions were added to existing uncontracted basis sets for K [118] and Rb [99]. The exponents were optimized to reproduce the experimental equilibrium bond length, r_e , and dissociation energy, D_e [119].

Our analysis is concentrated on the coplanar geometries of Fig. 4.1, which depicts a seemingly surprising result. While the top and middle panels depict the expected behavior of a repulsive and slightly attractive dipole-dipole interaction, respectively, the collinear geometry (bottom panel) reveals an unexpected barrier. The existence of this barrier can be traced to a strong repulsive quadrupole interaction. We also



Figure 4.1. KRb+KRb PES for coplanar geometries: aligned (top), T-oriented (middle), and collinear (bottom). The inset sketches the geometry: **R** joins the geometric center two KRb, θ_1 and θ_2 are the angles between their molecular axes and **R**, and ϕ is the angle between the molecular planes.

notice that it is higher (almost 7 K in height) than that of the aligned geometry (about 4 K). To better understand these *ab initio* results, we examine the KRb+KRb interaction in the long range region where the intermolecular wave function overlap is negligible and the interaction can be expressed by the long range expansion Eq.(2.2). The functions W_n , (as described formally by Eq.(2.18)) may contain electrostatic (*e.g.* dipole \mathcal{D} , quadrupole \mathcal{Q} , octupole \mathcal{O} , etc.) and/or dispersion and induction contributions $C_{n,i}$ [5, 72]. The first few terms are explicitly

$$\begin{split} W_{3} &= \mathcal{D}^{2} \left(2c_{1}c_{2} - s_{1}s_{2}c_{\phi} \right), \\ W_{4} &= \frac{3\mathcal{D}\mathcal{Q}}{2} \left(1 + 3c_{1}c_{2} - 2s_{1}s_{2}c_{\phi} \right) \left(c_{1} - c_{2} \right), \\ W_{5} &= \mathcal{D}\mathcal{O} \left\{ \frac{3}{2}s_{1}s_{2}c_{\phi} \left(2 - 5c_{1}^{2} - 5c_{2}^{2} \right) - c_{1}c_{2} \left(6 - 5c_{1}^{2} - 5c_{2}^{2} \right) \right\} \\ &- \mathcal{Q}^{2} \left\{ \frac{3}{2} \left(1 - 3c_{1}^{2} \right) \left(1 - 3c_{2}^{2} \right) - 12c_{1}c_{2}s_{1}s_{2}c_{\phi} + \frac{3}{4}s_{1}^{2}s_{2}^{2}c_{2\phi} \right\}, \\ W_{6} &= C_{6,0} + C_{6,1} \left(3c_{1}^{2} + 3c_{2}^{2} - 2 \right) + C_{6,2} \left(3c_{1}^{2} - 1 \right) \left(3c_{2}^{2} - 1 \right) \\ &+ C_{6,3}c_{1}c_{2}s_{1}s_{2}c_{\phi} + C_{6,4}s_{1}^{2}s_{2}^{2}c_{2\phi} \end{split}$$

where $c_i \equiv \cos \theta_i$, $s_i \equiv \sin \theta_i$, $c_{k\phi} \equiv \cos k\phi$. In Table 4.1, we list the corresponding parameters obtained by least squares fit of the PES up to n = 8. The fitted \mathcal{D} , \mathcal{Q} , and \mathcal{O} are also compared to *ab initio* values calculated at the all electron CCSD level of theory with the Roos ANO basis set [120]. \mathcal{D} and \mathcal{Q} agree to better than 1%, attesting to the accuracy of the PES, while \mathcal{O} is off by one order of magnitude, reflecting the small contribution of \mathcal{DO} in W_5 . Using Eq.(2.2), one can understand the physical origin of the barriers. For parallel molecules, *i.e.* $\theta_1 = \theta_2 \equiv \theta$ and $\phi = 0$, the two leading terms in V are

$$V(R,\theta) \simeq -\frac{W_3}{R^3} - \frac{W_5}{R^5}$$
 (4.1)

VD1 f4		AD		Φ	0	Ø	117	D	D
KRD fit		AB	r_e	D	Q	0	VV 6	$\kappa_{\rm sr}$	RQ
\mathcal{D}	0.234	KRb	7.69	0.234	16.99	-3.16	$18,\!528$	10.7	126
\mathcal{Q}	17.06	LiNa	5.45	0.246	10.56	-1.80	4,265	6.34	74.4
\mathcal{O}	-23.71								
$C_{6,0}$	11679	RbCs	8.37	0.554	14.19	-5.39	$26,\!599$	21.6	44.6
$C_{6,1}$	3182								
$C_{6,2}$	10441	LiRb	6.50	1.715	11.80	-1.61	8,528	9.95	12.0
$C_{6,3}$	-2893	LiCs	6.93	2.335	11.00	-7.26	$10,\!951$	12.7	8.5
$C_{6,4}$	158	NaK	6.61	1.199	12.91	3.83	9166	9.52	18.5

Table 4.1. Left: fit parameters (up to R^{-6}). Right, *ab initio* values of the equilibrium separation r_e , moments \mathcal{D} , \mathcal{Q} , and \mathcal{O} (from the geometric center), W_6 for the collinear orientation, and the turning points $R_{\rm sr}$, Eq.(4.3), and $R_{\mathcal{Q}}$, Eq.(4.5), for various molecules AB in v = 0 of $X^1\Sigma^+$. All values are in atomic units.

For collinear KRb, $\theta = 0$, with $W_3 = 2\mathcal{D}^2$ and $W_5 = -6\mathcal{Q}^2 + 4\mathcal{D}\mathcal{O} \simeq -6\mathcal{Q}^2$, and because of the relatively weak \mathcal{D} when compared to \mathcal{Q} , the long range attractive R^{-3} dipole interaction is overcome by a shorter-range repulsive R^{-5} quadrupole interaction (the attractive contribution of $\mathcal{D}\mathcal{O}$ is much weaker than that of the repulsive \mathcal{Q}^2); at shorter range still, the attractive R^{-6} and higher contributions dominate and bring V down, hence the barrier. For aligned KRb, $\theta = 90^{\circ}$, with $W_3 = -\mathcal{D}^2$ and $W_5 =$ $-(9/4)\mathcal{Q}^2 + 3\mathcal{D}\mathcal{O} \simeq -(9/4)\mathcal{Q}^2$, and the leading repulsive W_5 is about 3 times smaller than for the collinear case, hence the smaller barrier shown in Fig. 4.1.

Using Eq.(2.2), we study the geometries leading to a long range barrier; Fig. 4.2 depicts its height V_{top} as a function of θ_1 and θ_2 for a few twist angles ϕ . For $\phi = 0$, a substantial barrier exists along the diagonal $\theta \equiv \theta_1 = \theta_2$, for small angles ($\theta \sim 20^\circ$ or less), and for large angles ($\theta \sim 70^\circ$ or more). While the barrier remains present for the small angle cone ($\sim 20^\circ$) as ϕ increases, it quickly disappears for large θ . Roughly speaking, there is a barrier for a cone of $\theta \sim 20^\circ$ for any ϕ , and for larger molecular misalignment, the barrier vanishes. A significant barrier can thus be maintained by aligning the molecules within a small angular cone, allowing ultracold KRb samples



Figure 4.2. V_{top} vs. θ_1 and θ_2 . The main plot corresponds to a twist angle $\phi = 0$, while the two smaller plots to $\phi = 40^{\circ}$ (top) and 80° (bottom). V_{top} is set to zero if there is no barrier.

to remain stable and even be evaporatively cooled in various trap geometries (1-D when nearly collinear, and 1-D or 2-D when nearly aligned).

Polar molecules can be oriented by coupling rotational states along a polarizing external electric field **F**. This can be achieved by using a DC electric field; however the small dipole moment of KRb requires field strengths that are difficult to achieve in the laboratory. An alternative is to add a separate polarizing laser field [81] that directly couples the rotational states of the molecule. Although this utilizes a much smaller DC field, non-adiabatic effects are prominent [66], and for the sake of simplicity we calculate the rotational state coupling by increasing the DC external field. We start with a superposition of field-free symmetric top states, Eq.(2.36), labeled by their total angular momentum J with projection M along **F**. After transforming the moleculefixed frame potential $V(R, \theta_1, \theta_2, \phi)$ to the laboratory-fixed frame $V_{\text{Lab}}(\mathbf{R}, \hat{r}_1, \hat{r}_2)$ [121], the field averaged potential is found by evaluating Eq.(2.44) In Fig. 4.3, we illustrate the effect of **F** on a pair of KRb molecules in 1-D, with θ_F defined as the angle between F and R. For weak fields ($F \lesssim 10 \text{ kV/cm}$), the molecules remain largely in the first two (J = 0, 1) rotational states. Classically, they precess "wildly" on a wide cone about **F** averaging over a large range of relative angles, with the dominant contribution coming from the isotropic $C_{n,0}$ terms. This is depicted by the dashed lines in Fig. 4.3(a) for two orientations. In both cases, the interaction becomes strongly attractive at short distance, with the aligned geometry having a weak barrier (~ 1 mK) and the collinear case showing no sign of a barrier. The solid lines show the effect of a larger electric field where **F** strongly mixes more (~ 7) J's and strong barriers are present for both illustrated orientations. Fig. 4.3(b) shows the tightly aligned interaction for a range of θ_F near the aligned and collinear orientations, where we recover results similar to those in the molecular-frame. The barrier survives for a cone of angle θ_F of about 20° for both orientations, and the same conclusions about stability of 1-D and 2-D samples apply. For the aligned orientation, the barrier appears rapidly even for low fields, while larger fields ($F \gtrsim 70 \text{ kV/cm}$) are necessary for the collinear case (see Fig 4.3(c)). In both cases, the barrier grows rapidly to hundreds of mK, a value much higher than the typical kinetic energy of the trapped ultracold molecules (< 100 μ K).

Fig. 4.3(b) hints at the existence of a long range well for the collinear geometry. We analyze this well in the molecular-frame when the molecules are fully parallel $(\theta \equiv \theta_1 = \theta_2 \text{ and } \phi = 0)$. We find a long range well with several bound levels due to its breadth and the large mass of the KRb molecules. For $\theta = 0$, there are 7 levels, the deepest bound by ~ 2.7 mK with classical turning points at 110 and 205 a.u.. As θ increases, the R^{-5} repulsion gets smaller and the well deepens, and the binding energies increase accordingly until θ reaches $\theta_c \simeq 22^{\circ}$, at which point the barrier disappears (see Fig. 4.4(a)). We note that for a small deviation from $\theta = 0$, the



Figure 4.3. (a) KRb+KRb interaction (1-D) for weak (5 kV/cm: dashed lines) and strong electric fields (200 kV/cm: solid lines), for aligned (left) and collinear (right) orientations. The red cylinder represents the 1-D trap, the arrow the orientation of the field, and the sketch above the precessing molecules. (b) Intermolecular interaction with F = 200 kV/cm for the aligned (top) and collinear (bottom) geometries as a function of θ_F . (c) Height of the barrier for the aligned and collinear orientations as a function of F.

binding energies are not significantly affected, and an additional level v = 7 appears for $18^{\circ} < \theta < \theta_c$ (inset in Fig. 4.4(a)).

The variation of bound levels with θ affects the scattering between molecules and their effective interaction. Assuming θ (or θ_F) as a fixed external parameter, we estimate the *s*-wave scattering phase shift δ between two KRb molecules, which depends on the interaction V and the wave number k; $\delta < 0$ (> 0) corresponds to an effective repulsive (attractive) interaction. Here, we choose k assuming $\hbar^2 k^2 \sim m k_B T$ (m: mass of KRb; k_B : Boltzmann constant) for $T \simeq 700$ nK [38] and illustrate the effect in Fig. 4.4(b) in the molecule-frame. For small angles ($\theta \leq 14.7^{\circ}$), the interaction is attractive (with $\delta > 0$), while it becomes repulsive ($\delta < 0$) for larger angles. In an ideal 1-D trap, the repulsive barrier at $R \sim 100$ a.u. would stabilize the sample for an attractive effective interaction by preventing the molecules from reaching short distances where inelastic processes could take place. Larger angles would also give stable samples since the effective interaction is repulsive. By varying the orientation of the electric field with respect to the trap axis, the behavior of the sample could be controlled; an effective attractive interaction would lead to a dense self-trapped system, *i.e.* a liquid-like sample, while an effective repulsive interaction would give a dilute sample behaving like a gas. Such control could probe a quantum phase transition between a Luttinger liquid and an ultracold gas [54]. One could also create a chain of KRb molecules weakly bound together (e.q. by using photoassociation); these would be akin to ultracold polymer-like chains stabilized by an external electric field and a 1-D trap. We note that the effective interaction can also be controlled by varying the magnitude of **F**. In Fig. 4.4(c), we show δ for $\theta_F = 0$ as a function of F for two collision energies corresponding to 700 nK and 900 nK, and find that its sign can be changed by varying F.

Obtaining 1-D traps is challenging; assuming a harmonic trap in the perpendicular direction characterized by the frequency ω , the size of the ground state $a \sim \sqrt{\hbar/m\omega}$ is of the order of a few 1000 a.u. for optical traps. Molecules at densities of 10^{12} cm⁻³ loaded in such traps would be separated by roughly $d \sim 1 \mu$ m, and for repulsive effective interaction, the angle $\tan^{-1} a/d \leq 10^{\circ}$ between their axes would remain within the cone of stability. For an attractive effective interaction, the relevant angle is $\tan^{-1} a/R_Q$, where R_Q is the point where the barrier begins for two approaching molecules, which requires $a \sim 0.4R_Q = 50$ a.u. for KRb. Here, the sample would not be 1-D and inelastic processes allowed. Non-reactive species, such as RbCs, could be considered to prevent inelastic processes, or much tighter magnetic traps could be employed; in which case molecules in a triplet electronic state with a magnetic moment μ would be required. For KRb in its $a^{3}\Sigma^{+}(v = 0)$ state, $a \sim 60$ a.u. can be achieved [122], and with $R_{Q} \sim 150$ a.u. *, $\tan^{-1} a/R_{Q}$ would remain within the stability cone.

The features discussed here for KRb can be generalized to other polar molecules. The existence of a barrier for perfectly collinear molecules depends mostly on the first two terms of Eq.(2.2) (see Eq.(4.1)). By setting V = 0 and neglecting \mathcal{DO} , we find

$$R_{\mathcal{Q}} \simeq \sqrt{3\mathcal{Q}^2/\mathcal{D}^2},$$
 (4.2)

the point where the R^{-5} repulsion takes over the R^{-3} attraction. We can also define a point $R_{\rm sr}$ where the shorter range R^{-6} attraction takes over the R^{-5} repulsion, by neglecting the other contributions we obtain

$$R_{\rm sr} = -W_6/W_5. \tag{4.3}$$

If $R_{\mathcal{Q}}$ is outside the region where bonds are strongly perturbed or higher W_n terms do not contribute significantly ($R_{\rm sr} < R_{\mathcal{Q}} \lesssim 20$ a.u.), then the barrier may exist. We present the $R_{\mathcal{Q}}$ and $R_{\rm sr}$ values for various polar molecules in Table 4.1. Due to its large variance, \mathcal{D} dictates the $R_{\mathcal{Q}}$ behavior of the systems. Molecules with small \mathcal{D} (*e.g.*, LiNa and KRb) have a sizable $R_{\mathcal{Q}}$, and thus the existence of a barrier is very likely, unlike those with a large \mathcal{D} (*e.g.*, LiRb, LiCs and NaK). We also include RbCs, for which the existence of a barrier is uncertain. This is interesting since RbCs is known to not be reactive.

 $^{^{*}\}mathcal{D} = 0.017$ a.u. and $\mathcal{Q} = 1.47$ a.u. were computed consistently with the other methods in the text.



Figure 4.4. (a) Long-range well energy levels vs. θ ; an additional level v = 7 appears at 18° (inset). (b) scattering phase shift δ vs. θ for k corresponding to 900 nK for infinite F. (c) δ as a function of the field strength F for $\theta_F = 0$ at collision energies corresponding to 700 and 900 nK.
In conclusion, we find that the interaction between polar molecules exhibits a strong barrier when they are oriented about two specific geometries: aligned and collinear. We also show that the collinear setting gives meta-stable samples of ultracold molecules in a tight 1-D trap. The long range R^{-3} dipolar attractive and R^{-5} quadrupolar repulsive contributions in the collinear geometry lead to long range wells between polar molecules sustaining several bound levels. Varying the orientation of the molecules using an external electric field allows for non-trivial effects, such as changing the effective interaction from repulsive to attractive, and possibly the phase of the sample from gas to liquid. Finally, we also predict the existence of the collinear barrier for various bi-alkali polar molecules based on the relative strength of the dipole and quadrupole moments. The combination of available techniques to produce ultracold molecules [38, 42] and the ability to precisely control their spatial orientation [65, 66] provide the tools to investigate such systems.

4.2 External field alignment

Inclusion of just the quadrupole-quadrupole interaction to a dipole-dipole model can introduce significant changes in the form of potential energy barriers for collinear geometries ($\theta_1 = \theta_2 = \phi = 0$) at long range [7]. It is possible to estimate whether the inclusion of higher order electrostatic terms could lead to a barrier by introducing the outer zero energy turning point, R_q , which occurs when the R^{-5} repulsion overcomes the attractive R^{-3} dipole-dipole force. Keeping only the two leading terms in Eq.(2.18) and setting

$$E_{\rm int}(R_q, 0, 0, 0) = -\frac{\langle Q_{10} \rangle^2}{R_q^3} + \frac{3\langle Q_{20} \rangle^2 - 4\langle Q_{10} \rangle \langle Q_{30} \rangle}{R_q^5} = 0, \qquad (4.4)$$

we obtain



Figure 4.5. Dressed state electrostatic moments, $\langle Q_{L0}^{DS} \rangle$ (L = 1, 2, 3 corresponds to dipole, quadrupole and octopole moments respectively), of LiX as a function of an external DC electric field.



Figure 4.6. Dressed state electrostatic moments, $\langle Q_{L0}^{DS} \rangle$ (L = 1, 2, 3 corresponds to dipole, quadrupole and octopole moments respectively), of NaX, KX and RbCs (X=Na,K,Rb,Cs as appropriate) as a function of an external DC electric field.

$$R_q = \frac{\sqrt{3\langle Q_{20}\rangle^2 - 4\langle Q_{10}\rangle\langle Q_{30}\rangle}}{\langle Q_{10}\rangle}.$$
(4.5)

When this outer turning point is sufficiently long range $(R_q \gtrsim 20 \text{ a.u.})$ the introduction of these higher order terms can be important and lead to long range barriers [7], and thus should be examined in further detail *.

^{*}It should be reiterated that from an alignment point of view, obtaining field-dressed electrostatic moments sizeable enough to produce long range barriers requires electric field strengths that are experimentally intractable ($F \gtrsim 30 \text{ kV/cm}$). However from a molecule-fixed-frame collision point of view the merits of including these electrostatic moments is then independent of the external field strength and Eq.(4.5) should then be referenced.

In evaluating the field coupling and alignment of the various alkali diatomic molecules, the rotational wavefunction expansion is greatly simplified by making use of the initial premise that the molecules are in the ro-vibrational ground state. As such $\Omega \equiv 0$ and M = 0 (the use of a DC external field will not mix different M values), reducing both Eq.(2.43) and (2.47) significantly. In Fig. 4.5 and 4.6 we have plotted the DC field dressed electrostatic moments as a function of the external field strength. While the very high field strengths in Fig. 4.5 and 4.6 are generally experimentally challenging, it is illustrative to show how difficult it is to obtain both strong orientation ($\langle \cos \theta \rangle > 0.85$) and alignment ($\langle \cos^2 \theta \rangle > 0.85$) in molecules with small rotational constants, regardless of the strength of the dipole moment. It is also instructive to examine the low-field strengths of Fig. 4.5 and 4.6, where the linear trend of each curve on the log-log scale shows the general scaling of the static moments as a function of the external field as discussed in Sec. 2.4. In Fig.4.7 we have evaluated Eq.(2.43) for KRb (KRb is chosen for its medium strength dipole moment and large rotational constant) at various DC field strengths. This is done by numerically diagonalizing Eq.(2.38) for each field strength F to obtain Eq.(2.46). After which Eq.(2.43) can evaluated for any inter-molecular distance **R**. In diagonalizing Eq. (2.38) a question of the size of the rotational basis set expansion in Eq.(2.36) arises. Performing a convergence test, it was determined that including between 15 to 30 rotational states in the expansion is sufficient for all the molecules studied. Examining Fig.4.7, the difference between the low and high field strengths is easily identified by the change in behavior from most similar to the field free case (e.g. isotropic contributions dominate the interaction potential) to the regime where the dressed state van der Waals interaction energy more closely resembles the molecule-fixed frame van der Waals potential (e.g. when electrostatic contributions become key). This high field strength regime is more quantitatively defined when both $\langle \cos \theta \rangle$ and $\langle \cos^2 \theta \rangle$ is greater than



Figure 4.7. DC field coupled van der Waals curves (Eq.(2.43) with $M_i = M'_i = 0$) of ⁴⁰K⁸⁷Rb for both low and high fields as well as the approximate two-state van der Waals curve (Eq.(2.55)). Here $F \sim 20$ kV/cm is the intermediate field strength where more than two rotational states begin to strongly couple.

0.9 (which corresponds to roughly seven strongly coupled rotational states). Also in Fig.4.7 the approximate two-state model of Eq.(2.55) can be seen to agree very well with the fully coupled equations in the low-field limit.

4.2.1 Optical pumping

The generality of Eq.(2.44) through the arbitrariness of the choice of rotational state density adds flexibility to the applications studied beyond that of the external field control of sections 2.4, 4.1 and 4.2. The idea comes from a simplification of

ΔJ	ΔM	\tilde{W}_{nLM_L}	M_L
1	0	$\tilde{W}_{32M_L}, \tilde{W}_{54M_L}$	$\{0\}, \{0\}$
1	1	$\tilde{W}_{32M_L}, \tilde{W}_{54M_L}$	$\{-2, 0, 2\}, \{0\}$
2	0	\tilde{W}_{54M_L}	$\{0\}$
2	2	\tilde{W}_{54M_L}	$\{-4, -2, 0, 2, 4\}$

Table 4.2. Non-zero electrostatic long range coefficients from evaluating Eq.(2.44)

the schemes for alignemnt/orientation control put forward by Härtelt *et al.* [81], Holmegaard *et al.* [65] and Nielsen *et al.* [66], where the static alignment field is removed and only optical pumping of rotational states is performed. In doing so it is possible to engineer rotational state densities (Eq.(2.46)) by choosing which states are populated in the dressed state basis, Eq.(2.36). The motivation laying behind this can be seen directly when the Three-J symbols in Eq.(2.45) are examined, where it is observed that the nonzero contributions to \tilde{W}_{nLM_L} are restricted by the selection rules for (J', L_i, J) . Thus the nonzero contributions to \tilde{W}_{nLM_L} can be controled by careful choice of rotational states. The various two state combinations and their subsequent effect on the long range contributions are listed in Table 4.2.

Chapter 5 Alkali cluster thermochemistry

5.1 Potential energy surface of the $1^2A'$ Li₂+Li doublet ground state*

With the success of ultracold molecular formation among the alkali metals over the past decade via photoassociation [20] and more recently with Feshbach resonances [21], the dynamics of molecules in ultracold traps have become an important topic to many physicists. Alkali dimers have been formed in many different homonuclear and heteronuclear configurations, for both singlet and triplet ground electronic states. Furthermore, recent experiments using KRb [34–36] have shown the possibility of efficiently forming ultracold ground vibrational state diatoms. While both ground and excited singlet and triplet states of alkali diatoms have been studied extensively both experimentally and theoretically, alkali trimers have generally been ignored by both theorists and experimentalists alike. In the last few years there has been an increase of interest in few-body physics with continued success in the cooling and trapping of atoms.

We describe in this section the calculations we have done on both the $1^2A'$ and $1^2A''$ surfaces of the lithium trimer and future goals for the use of these surfaces. In this work, all calculations have been done using the MOLPRO 2008.1 quantum chemistry package [123] unless otherwise stated. To accurately describe dissociation

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Orbital Type	SBK	LFK	Scaled LFK
s	0.6177000	0.6177000	0.52504500
	0.1434000	0.1434000	0.12189000
	0.0504800	0.0504800	0.04290800
	0.0192300	0.0192300	0.01634550
p	0.6177000	0.6177000	0.00690155
_	0.1434000	0.1434000	0.64858500
	0.0504800	0.0504800	0.15057000
	0.0192300	0.0192300	0.05300400
		0.0065729	0.02019150
d		0.1346266	0.13799227
		0.0546860	0.05605315
		0.0180355	0.01848639
		0.0076882	0.00788041

Table 5.1. Uncontracted basis set exponents for for the Stevens, Basch and Krauss lithium pseudopotential basis used in this work. The s, p and d orbital exponents are each scaled to give an optimal dissociation energy for Li₂ as discussed in the text.

energies, equilibrium geometries and vibrational frequencies in alkali-metal clusters, it is necessary to account for the electronic core-valence (CV) correlation energy [124]. For all electron calculations this is possible for the lighter alkali atoms (Li through K) by using the explicitly correlated basis of Iron, Oren and Martin (IOM) [86]. This approach has recently been done by Cvitaš *et al.* [125] for the spin aligned $1^4A'$ Li₃ surface using spin restricted coupled cluster calculations with single, double and iterative triple excitations (RCCSD(T)). To account for CV correlation in heavier atoms, where all electron calculations are prohibitively expensive, it is necessary to use a core polarization potential (CPP). This is also necessary for valence electron full configuration interaction (FCI) calculations where an ECP (a physically equivalent representation to the frozen core approximation which has no CV correlation) is substituted for the atomic electrons. This method has been used with great success for calculating both lithium dimer potential curves [126] and trimer potential surfaces of potassium [127]. The theoretical description of the CPP is a straightforward addition to that of the ECP model of atomic cores. In the Born-Oppenheimer approximation the nonrelativistic molecular Hamiltonian can be separated into kinetic and interaction operators T and V respectively. Approximating the core of each nuclei with an l dependent pseudopotential and including the polarization effects at the nuclei gives for the interaction operator

$$V = \sum_{k} (V^{k} + V_{cpp}^{k}) + \sum_{j>i} \frac{1}{r_{ij}} + V_{cc},$$
(5.1)

where

$$V^{k} = \sum_{i} -\frac{Q_{k}}{r_{ik}} + \sum_{il} B^{k}_{il} exp(-\beta^{k}_{il} r^{2}_{il}) P^{k}_{l}$$
(5.2)

is the core pseudopotential,

$$P_l^k = \sum_m |klm_l\rangle \langle klm_l| \tag{5.3}$$

is the projection operator onto the subspace of angular momentum l on core k and V_{cc} is the core-core coulomb interaction. Here the polarization potential, V_{cpp}^k for a given core k, is expressed in terms of a static polarizability and external field at the nuclei position by

$$V_{cpp}^{k} = -\frac{1}{2}\alpha_{k}\mathbf{F}_{k}\cdot\mathbf{F}_{k}.$$
(5.4)

where the electric field \mathbf{F}_k at core k arising from the coulomb interaction with the electrons at \mathbf{r}_{ki} and other cores at \mathbf{R}_{kj} is

$$\mathbf{F}_{k} = \sum_{i} \frac{\mathbf{r}_{ki}}{r_{ki}^{3}} C(r_{ki}) - \sum_{j} \frac{Z\mathbf{R}_{ki}}{R_{ki}^{3}}.$$
(5.5)

Method/Basis	r_e [Å]	$\omega_e [\mathrm{cm}^{-1}]$	$D_0 [{\rm cm}^{-1}]$	$D_e \ [\mathrm{cm}^{-1}]$
Expt.[129]	2.673	351.43	8434.58	8516.36[130]
Recommended	2.667	352.98	8340.12	8516.43
FCI/SBK scaled LFK	2.693	346.54	8198.85	8371.83
FCI/SBK+CPP LFK	2.663	353.89	8338.45	8515.10
FCI/SBK LFK	2.687	347.19	8197.18	8371.04
RCCSD(T)/CVQZ[86]	2.676	353.05	8294.15	8470.27
RCCSD(T)/CV5Z[86]	2.674	353.08	8311.70	8488.46

Table 5.2. Comparison of different spectroscopic constants of Li_2 using benchmark basis sets with both explicit inclusion of core-valence correlation in RCCSD(T) calculations or through the empirical contribution through a core polarization potential with valence electron full configuration interaction.

The value of the static polarizability for Li⁺ is $\alpha_k = 0.1915a_0$ [116] and the cutoff function $C(r_{ki})$ defined by Fuentealba *et al.* [116] is given as

$$C(r_{ki}) = (1 - e^{-(\delta_k r_{ki})}), \tag{5.6}$$

with the cutoff parameter chosen to be $\delta_k = 0.831 a_0^{-2}$ [116]. This form of the cutoff parameter was first presented by Müller *et al.* [128] and produces good agreement for ground and low excited states, however it does show diminished results for Rydberg states [128]. Our calculations using this core polarization potential to describe the core valence correlation energy were done using the MOLPRO 2008.1 [123] implementation of the Fuentealba *et al.* [116] CPP.

Atomic and molecular polarizabilities are important factors for long range interatomic and molecular interactions. In ultracold systems this is a dominant contribution to the scattering length in addition to the location of the inner wall. To accurately describe both of these quantities in the lithium trimer, we require that the basis set be flexible enough to describe atomic polarization at long range while accurately representing the inner wall. Very accurate polarizability calculations require an accurate description of electron correlation and a large basis set containing diffuse functions such as the Sadlej basis sets [131, 132], but this is computationally impractical to implement for large all electron systems. Accurate polarizability calculations can be achieved using an ECP with a small but well chosen basis set as demonstrated by Labello, Ferreira and Kurtz (LFK) [133, 134]. Their basis set augments the Stevens, Basch and Krauss (SBK) ECP basis [135], with an additional p function and four extra d functions optimized following the Sadlej [131, 132] method.

Using the SBK pseudopotential, we further optimized the uncontracted LFK basis (see Table 5.1 for the exponents) with and without the CPP for the Li₂ $X^{1}\Sigma_{g}^{+}$ ground state. This was done using three scale factors $\beta_{\lambda}(\lambda = s, p, d)$ optimized at the FCI level to give the best calculated value of the dissociation energy. As a benchmark, the CVQZ and CV5Z IOM basis [86] at the CCSD(T) level correlating all electrons (no frozen core) gives an error in the calculated dissociation energy of 46.087 cm⁻¹ and 27.902 cm⁻¹ respectively, while at the valence FCI level the unscaled LFK basis the error is 1.25 cm⁻¹. Optimizing the β_{λ} coefficients to give the best dissociation energy, we obtain a difference of 0.077 cm⁻¹ using the scaled exponents listed in Table 5.1, corresponding to the scale factors $\beta_{s} = 0.85$, $\beta_{p} = 1.05$ and $\beta_{d} = 1.025$. In Figure 5.1 and Table 5.2 the results from the different basis functions and methods can be seen compared to the Rydberg-Klein-Rees (RKR) curve adjusted to reproduce the ultracold scattering results. We chose to use this scaled, uncontracted LFK basis with the SBK ECP and Fuentealba CPP in calculating the potential energy surface of the lithium trimer at the FCI level of theory.

Calculations of *ab initio* points at the FCI level are very computationally intensive, even for three electrons with the compact basis just described, so to accurately describe an entire potential energy surface with a low density of *ab initio* points we implemented the global IMLS fitting method [136]. In this method the potential energy at an arbitrary point Z in the (x, y) plane is approximated by the use of a linearly



Figure 5.1. Benchmark singlet Li_2 potential energy curves using both the corevalence correlation consistent basis sets of Iron, Oren and Martin and core polarization potential Stevens, Basch and Krauss pseudopotential with an extended and scaled ECP basis set calculated at the RCCSD(T) and full configuration interaction level of theory respectively. The scattering RKR curve is the inner wall shifted version of Côté *et al.* such that the potential predicts the correct scattering lengths and Feschbach resonances.



Figure 5.2. Molecule frame Jacobi coordinates are used to describe the lithium trimer geometry. Within this coordinate system the potential energy surface is calculated assuming that the lithium dimer bond r_e is adiabatically relaxed as the colliding lithium atom approaches.

independent basis $b_j(Z)$ (j = 1, ..., n) and expansion coefficients $a_j(Z)$ (j = 1, ..., n)so that the interpolated energy is given by

$$V_{int}(Z) = \sum_{j}^{n} a_j(Z) b_j(Z).$$
(5.7)

The expansion coefficients $\mathbf{a}(Z)$ are found by minimizing the error function

$$E(V_{int}) = \sum_{j=1}^{N_d} w_j(Z) \left(\sum_{i=1}^n a_i(Z) b_i(Z) - f_j(\ell_j) \right)^2$$
(5.8)

of the interpolated energy V_{int} and the *ab initio* energy $f_i(\ell_i)(i = 1, ..., N_d)$ at coordinates ℓ_i where N_d is the number of *ab initio* data points.

Expressing the solution to the normal equations $\partial E(V_{int})/\partial a_j = 0$ in matrix form we obtain the linear equation for the expansion coefficients [136]

$$BW(Z)B^{T}\mathbf{a}(\mathbf{Z}) = BW(Z)\mathbf{f},$$
(5.9)

where W(Z) is the diagonal matrix of weights $w_i(Z)$ and B is the matrix

$$B = \begin{pmatrix} b_1(\ell_1) & b_1(\ell_2) & \cdots & b_1(\ell_{N_d}) \\ b_2(\ell_1) & \ddots & b_2(\ell_{N_d}) \\ \vdots & \ddots & \vdots \\ b_n(\ell_1) & b_n(\ell_2) & \cdots & b_n(\ell_{N_d}) \end{pmatrix}.$$
 (5.10)

The linear system in Eq. 5.9 is routinely ill conditioned and so is solved by singular value decomposition.

The weights $w_i(Z)$ dictate the effective range at which a given *ab initio* point will contribute to the global fit and the effective contribution to the fit. We use Guo *et al.*'s [137] form of the weight function, which introduces a cutoff function $S(\chi)$ to the unnormalized weight function $v_i(||Z - \ell_i||)$ so as to smoothly go to zero at a given cutoff radius R_{cut} . The cutoff function is given [137] by

$$S(\chi) = \begin{cases} (1 - \chi^m)^4 & \text{if } 0 \le \chi \le 1, \\ 0 & \text{if } \chi > 1, \end{cases}$$
(5.11)

with m = 10 and the unnormalized weight function is

$$v_i(Z) = \frac{exp[-\|Z - \ell_i\|^2/\zeta^2]}{(\|Z - \ell_i\|/\zeta)^4 + \epsilon}$$
(5.12)

where $\epsilon = 10^{-10}$ removes the singularity at ℓ_i . Then the normalized weight function is

$$w_i(Z) = \frac{S(\|Z - \ell_i\|^2 / R_{cut}) v_i(Z)}{\sum_j^{N_d} S(\|Z - \ell_i\|^2 / R_{cut}) v_j(Z)},$$
(5.13)

where R_{cut} is to be determined as to give the best fit. Finally the basis functions are chosen to be bivariate polynomials of order n = 6 such that

$$b(Z) = 1, Z_1, Z_2, Z_1^2, Z_2^2, Z_1 Z_2, \dots, Z_1^{n-1} Z_2, Z_1 Z_2^{n-1},$$
(5.14)

where the inverse coordinates $Z_i = 1/x_i$ are used in this work. With the choice of coordinates used here there is a coordinate singularity in C_{2v} symmetry. To avoid this all coordinates x_i are shifted by the same positive, arbitrary additive factor for the fit then transformed back upon completion. The scaling parameter ζ was chosen to be the average distance between the interpolant point Z the *ab initio* points. With this definition the cutoff radius was defined in terms of ζ as $R_{cut} = 50.0 * \zeta$. This interpolant method is used for the lithium trimer $1^2A'$ PES to obtain a global fit using a low number of *ab initio* points as references.

The $1^2A'$ surface of Li₃ was calculated at the full configuration interaction level using the scaled LFK basis set, the SBK pseudopotential [135] and core polarization potential described above, with the three valence electrons included in the FCI calculation. At the FCI level, there are 410670 configurations of A' symmetry and 383292 configurations of A'' symmetry. All FCI calculations were performed with the Knowles-Handy determinant FCI program [138, 139] using the MOLPRO 2008.1 package [123]. The geometry was chosen so to best describe the diatomic-atomic collision process. As such we used the molecular frame Jacobi coordinates for a homonuclear system where we define a vector r_e along the diatomic inter-nuclear axis and another vector R_C from the diatomic center of mass to the colliding atom where the collision angle A is defined from the $C_{\infty v}$ axis (see Figure 5.2). With this coordinate system the most efficient grid of *ab initio* points is an evenly spaced angular grid with the radial grid chosen to have the highest density of points at the minima. We calculated 26 points with the collision angle varying between 90° and 45° on the $1^2A'$



Figure 5.3. Near equilibrium geometry potential energy surface for the Li₃ $1^2A'$ electronic state calculated using valence electron full configuration interaction theory. Equilibrium is found to be at bond lengths of $r_e = 3.218$ Å and $R_C = 2.238$ Å for C_{2v} geometry configuration.

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Figure 5.4. First four Li₃ doublet states in C_{2v} symmetry near the 1^2A_1 state equilibrium. A conical interesction is observed at $R_C = 2.51$ Å between the 1^2A_1 and 1^2B_2 states with a further Li₃ minimum seen near $R_C = 2.25$ Å for the 1^2B_2 state.

Li₃ surface by choosing A and R_C then optimizing the dimer bond length to give the lowest energy configuration. The $1^2A'$ state is found to have a triangular equilibrium geometry on the 1^2A_1 surface with $r_e = 3.218$ Å and $R_C = 2.238$ Å for the Jacobi bond lengths with a dissotiation energy of 4979.42 cm⁻¹. The interpolated surface near the equilibrium geometry is show in Figure 5.3.

We have investigated the lowest states of ${}^{2}A_{1}$, ${}^{2}B_{1}$ and ${}^{2}B_{2}$ symmetry and the first excited ${}^{2}A_{1}$ state in point group C_{2v} using the complete active shell (CAS) method in conjunction with FCI. The same SBK and CPP representation of the core as in the FCI calculation of the $1{}^{2}A'$ surface was used here with an active space of 12 orbitals $(5a_12b_24b_21a_2)$ for the energies of the 1^2A_1 , 1^2B_1 , 1^2B_2 and 2^2A_1 states as seen in Figure 5.4. Here R_C is fixed and r_e is optimized at the CAS level with tight convergence. This is followed by a FCI calculation to obtain the energy at this geometry, with typical errors in the CAS geometry optimization compared to that of the FCI geometries on the order of a mÅ. A conical intersection between the 1^2A_1 and 1^2B_2 surfaces is observed at $R_C = 2.51$ Å which is the result of Jahn-Teller splitting of the $1^2E' D_{3h}$ surface [140].

Preliminary calculations of the Li₃ $1^2A''$ surface have been carried out using second order spin restricted open-shell Møller-Plesset perturbation (ROMP2) theory as implemented in Gaussian 03 [141]. Here the IOM CVTZ basis set [86] was used for calculation size convenience, with a benchmark diatomic bond length error of 0.075Å at ROMP2 and 0.008Å at RCCSD(T). The analytic potential energy surface was interpolated using cubic splines with 256 *ab initio* data points and is shown in Figure 5.5. This $1^2A''$ state has a dissociation energy of 14156.5 cm⁻¹ at the equilibrium triangular geometry of $R_C = 2.40$ Å and $r_e = 2.77$ Å in C_{2v} .

The electronic $1^2 A'$ ground state surface of the lithium trimer has been calculated using valence electron FCI theory with the lithium cores represented using the SBK pseudopotential [135]. It was found to be necessary to systematically include corevalence correlation in the calculation for precise calculations of diatomic spectroscopic values. The basis set chosen is a p and d function augmentation of the SBK basis set [135] as given by Labello, Ferreria, and Kuntz [133] with the s, p and d functions optimized with the inclusion of a core polarization potential to predict the correct diatomic dissociation energy. With the recommended basis set of this work, the use of the core polarization potential to include core-valence effects lead to an improvement of 26.4 mÅ in the bond length, 6.44 cm⁻¹ of the vibrational frequency and 144.605 cm⁻¹ dissociation energy of Li₂.



Figure 5.5. The Li₃ $1^2 A''$ potential energy surface calculated at the second order spin restricted open-shell Møller-Plesset perturbation theory for collision angles 90° (C_{2v}) to 45°. The dissociation energy is 14156.5cm⁻¹ with $R_C = 2.40$ Å and $r_e = 2.77$ Å in the C_{2v} symmetry.

To interpolate between sparse *ab initio* data points, the full interpolant moving least squares method was implemented using a scaled exponential weighting function with a smooth cutoff function as a constraint on the number of included data points. The surface was expanded using the inverse spatial coordinates with a 6 order bivariate polynomial. With this interpolation method the $1^2A'$ surface was calculated for collision angles 45° to 90° near the equilibrium Jacobi bond lengths of $r_e = 3.218$ Å and $R_C = 2.238$ Å. A conical intersection is found between the 1^2A_1 and 1^2B_2 states in C_{2v} symmetry near the equilibrium geometry of the $1^2A'$ surface^{*}. Because of the location of this intersection it is necessary to account for its existence in both chemical and ultracold physics. A preliminary surface for the excited state $1^2A''$ is also presented at the ROMP2 level of theory. It is the authors intention to continue to study the long range interactions of the lithium trimer on the ground $1^2A'$ surface and to investigate both elastic collisions and photoassociation of the lithium diatom-atom pair for the formation of ultracold trimers.

^{*}It should be noted that the global minimum of the $1^2A'$ surface correlates to the 1^2B_2 state, and not the expected 1^2A_1 curve.



Figure 5.6. Schematic geometries of the D_{2h} and C_s stable tetramer structures.

5.2 Structure and thermochemistry of K_2Rb , KRb_2 and $K_2Rb_2^*$

Theoretical work on electronic structure of few-body alkali systems has been limited to lighter homonuclear trimers, in particular doublet [8] and quartet [125] Li₃, doublet K₃ [127] and quartet Na₃ [142]. The recent work of Żuchowski and Hutson [67] has characterized the atomization energy of the alkali homo- and heteronuclear triatomic species formed from Li, Na, K, Rb, and Cs. These homonuclear trimers have ²A' ground electronic states in C_s symmetry that correlate to B_2 symmetry in C_{2v} . Previous mixed alkali tetramer studies have been limited to structure studies of Li_nX_m (X=Na and K) [143, 144] and that of RbCs+RbC_s [109]. To date only the calculations of Byrd *et al.* [10, 11] have been reported for the heteronuclear K_nRb_m tetramer molecules.

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	r_e				
K_2	3.956				
Rb_2	4.233				
KRb	4.160				
	$r_{\rm K-Rb}$	$r'_{\rm K-Rb}$	θ		
$K_2Rb C_{2v}$	4.279	4.279	70.68		
$K_2Rb C_s$	4.361	5.234	48.81		
$\operatorname{KRb}_2 C_{2v}$	4.271	4.271	82.13		
$\operatorname{KRb}_2 C_s$	4.193	5.179	57.07		
	$r_{\rm Rb-Rb}$	$r_{\rm K-K}$	$r_{\rm K-Rb}$	$ heta_{ m K-Rb-Rb}$	$\theta_{ m K-K-Rb}$
$K_2Rb_2 D_{2h}$	8.224	4.0307	4.579		
$K_2Rb_2 C_s$	4.761	4.408	4.189	53.34	55.476

Table 5.3. Calculated CCSD(T)/QZVPP molecular geometries (in Angstroms and degrees).

Electronic structure calculations were performed on K_2 , Rb_2 , KRb, K_2Rb , KRb_2 , and K_2Rb_2 at the CCSD(T) [96, 145] level of theory. As core-valence effects can be important in alkali metals, we correlate the inner valence electrons in potassium, keeping only $1s^22s^22p^2$ in the core. Rubidium is heavy enough that relativistic effects are significant, so we replace its inner shell electrons by the Stuttgart small-core relativistic ECP (ECP28MDF) [146]. Basis sets are taken from the Karlsruhe def2-TZVPP [147] and def2-QZVPP [84] orbital and fitting sets as discussed in Chapter 3.

Optimized geometries for K₂, Rb₂, KRb, K₂Rb, KRb₂, and K₂Rb₂ were found at the CCSD(T)/def2-TZVPP level of theory. Calculation of the harmonic vibrational frequencies was done to verify that the calculated structures were minima on the potential energy surface, and the calculated frequencies were used to obtain vibrational zero point energy (ZPE) corrections. These structures were further optimized at the CCSD(T)/def2-QZVPP level of theory, leading to a 0.07 Å correction in the bond lengths and 60 cm⁻¹ in final atomization energies. The CCSD(T)/def2-QZVPP geometries are tabulated in Table 5.3.

	ZPE TZVPP	D_e TZVPP		$D_e \; \mathrm{QZVPP}$		$D_0 ext{ CBS}$	
	$\operatorname{CCSD}(T)$	$\operatorname{CCSD}(T)$	CCSD(T)-F12b	$\operatorname{CCSD}(T)$	CCSD(T)-F12b	$\operatorname{CCSD}(T)$	CCSD(T)-F12b
$\mathrm{K}_{2}{}^{a}$	46.0	4098.8	4276.9	4460.0	4369.7	4677.6	4391.5
$\mathrm{Rb}_2{}^b$	26.8	3494.3	3723.3	3842.7	3885.4	4070.2	3976.8
KRb^{c}	35.4	3829.4	4015.6	4135.6	4128.7	4323.6	4175.7
$K_2 Rb C_{2v}$	69.8	5588.2	5805.5	6067.7	5995.7	6574.2	6009.4
$K_2Rb C_s$	72.4	5606.3	5843.7	6179.1	6015.9	6524.7	6069.1
$\operatorname{KRb}_2 C_{2v}$	62.8	5394.5	5635.1	5911.0	5842.2	6043.5	5788.3
$\operatorname{KRb}_2 C_s$	59.0	5215.9	5475.4	5728.5	5690.4	6225.1	5930.5
$K_2Rb_2 D_{2h}$	129.5	10210.8	10669.4	11275.3	11011.1	11922.7	11131.0
$K_2Rb_2 C_s$	126.2	10198.3	10629.9	11211.4	10993.7	11824.6	11133.0

Table 5.4. Dissociation and zero point energies calculated using CCSD(T) and CCSD(T)-F12b correlation methods with successive basis sets and CBS extrapolated values (in cm⁻¹).

^{*a*}Experimental value 4405.389 cm⁻¹[148].

^bExperimental value 3965.8 cm⁻¹[149].

^cExperimental value 4180.417 cm⁻¹[35].

Evaluation of the contribution of scalar relativistic corrections to K_2 indicate a small 0.005 Å and $< 8 \text{ cm}^{-1}$ contribution in all electron correlation calculations [86], while for Rb₂ it has been shown [150] that the small core Stuttgart pseudopotential gives an accurate representation of relativistic effects on the bond length and dissociation energy.

Single point energy calculations were then done using the CCSD(T)-F12b [110, 111] (explicitly correlated CCSD(T)) level of theory. The use of explicitly correlated methods accelerate the slow convergence of the one-particle basis set by including terms containing the inter-electron coordinates into the wavefunction [151], thus yielding very accurate results using triple and quadruple zeta basis sets. In addition, we estimate the complete basis set (CBS) limit using the two-point extrapolation formula of Helgaker *et al* [152]

$$E_{\rm CBS} = \frac{n^3 E_n - (n-1)^3 E_{n-1}}{n^3 - (n-1)^3}.$$
(5.15)

In Table 5.4 the CCSD(T) and CCSD(T)-F12b dissociation energies for the def2-TZVPP and def2-QZVPP basis sets are tabulated as well as the zero point energy (ZPE) corrected atomization energies. After extrapolation, the diatomic CCSD(T)-F12b ZPE corrected dissociation energies agree very well with the experimental diatomic dissociation energies, as shown in Table 5.4. The *ab initio* calculations were done using the Gaussian 09 [153] and MOLPRO [115, 123, 154] packages.

We have found that both K₂Rb and KRb₂ have two energetically close local minima on the ground state surface, one of C_{2v} symmetry and another less symmetric C_s structure (geometries given in Table 5.3). While dependent on the level of theory used to evaluate the atomization energy, we conclude that the symmetric C_{2v} geometry is the global minima for each trimer. The atomization energies calculated are found to be in good agreement with those recently published by Żuchowski and Hutson [67]. The K₂Rb₂ tetramer is found to have two nearly degenerate minima on the potential energy surface. One is a rhombic structure of D_{2h} symmetry, and another planar (C_s) structure that corresponds to an interchange of K and Rb atoms. These structures are bound by ~ 3000 cm⁻¹ with respect to K₂+Rb₂ or KRb+KRb. The electronic structure of these two isomers is very similar, and their stability is likely due to three-center bonds of the sort proposed for Li_nNa_{4-n} clusters [143, 144]. The rhombic K₂Rb₂ structure has a short (~ 4Å) distance and a long (~ 8Å) Rb-Rb distance.

To determine if there is any barrier to the KRb+KRb \rightarrow K₂Rb₂ \rightarrow Rb₂+K₂ reaction, we calculate a minimum energy path for the KRb+KRb \rightarrow K₂Rb₂ and $Rb_2 + K_2 {\rightarrow} K_2 Rb_2$ reactions. We start by locating the minimum energy geometric configuration at long range. This is done by calculating *ab initio* the dipole and quadrupole electrostatic moments of K_2 , Rb_2 and KRb and then minimizing the long range electrostatic interaction energy [70] with respect to the angular configuration of the molecules. This minimization resulted in a T type geometry for both K_2+Rb_2 and KRb+KRb. We have recently shown that long range expansions of this type accurately reproduce diatom-diatom interaction energies [3]. From these initial geometries, the reaction path was followed by freezing the diatom-diatom distance and optimizing the diatomic bond lengths and angular orientations at the frozen core CCSD(T)/def2-TZVPP level of theory. Single point energies were evaluated along this path using the CCSD(T)-F12b level of theory including the core-valence correlation energy and extrapolated to the CBS limit as discussed above. This procedure, in which a high level energy profile is evaluated along a reaction path calculated at a lower level of theory, is known to be a good approximation to the energy profile along the reaction path calculated at the high level of theory [155].

We find that the KRb+KRb dissociation limit connects to the D_{2h} minima while the K₂+Rb₂ dissociation limit connects to the C_s minima, with no barrier found to either reaction. A similar conclusion was obtained for the RbCs+RbCs \rightarrow Rb₂+Cs₂ reaction by Tscherbul *et al* [109]. To finish characterizing the reaction path going from one dissociation limit to the other, we locate the transition state and calculate the intrinsic reaction coordinate (IRC) [156] reaction path connecting the C_s and D_{2h} minima structures at the same level of theory as describe above. Optimizing the transition state geometry at the inner valence CCSD(T)/def2-TZVPP discussed previously and evaluating an accurate atomization energy using our CCSD(T)-F12b prescription we find that the transition state is 1167.3 cm⁻¹ above the D_{2h} dissociation energy. The calculated reaction path is plotted in Figure 5.7 using the approximate reaction coordinate

$$\Delta R = \frac{1}{2} (R_{\rm K-K} + R_{\rm Rb-Rb}) - \frac{1}{2} (R_{\rm K-Rb} + R'_{\rm K-Rb})$$
(5.16)

where R_{A-B} is the distance between atoms A and B.

The formation and trapping of rovibrational ground state KRb diatoms with a high phase space density [35] offers the opportunity to study chemical reactions in the ultra-cold regime [157]. As seen in Figure 5.8, the three-body reaction KRb+Rb \rightarrow Rb₂+K is energetically forbidden at ultra-cold temperatures, leaving the endothermic four-body reaction KRb+KRb \rightarrow Rb₂+K₂ as the only pathway to forming Rb₂ within the trap. Measurements of the population of Rb₂ within the trap will then allow direct probing of the exchange reaction rate of KRb+KRb. Inherent in this exchange reaction is the possibility of studying the role of fermionic/bosonic spin statistics in ultra-cold chemical reactions [158–164]. In this temperature regime, *s*-wave scattering of fermionic ⁴⁰KRb is suppressed which should greatly diminish the reaction rate of ⁴⁰KRb+⁴⁰KRb, thus leaving the trap stable to four-body losses. If instead the trap



Figure 5.7. Minimum energy path connecting the KRb+KRb and K_2 +Rb₂ dissociation limits. Included are schematic geometric at points of interest, where open and closed circles represent rubidium and potassium atoms respectively.



Figure 5.8. Schematic energy level diagram for fragment and structure energies involving KRb with KRb and separated atoms. Inset figure shows the small difference between the KRb+KRb and K_2 +Rb₂ asymptotes.

was formed with bosonic ³⁹KRb or ⁴¹KRb molecules, no such collisional suppression is expected, where we then expect comparably large reaction rates to occur. It is also possible to explore recent theoretical predictions [164] which show that if a bosonic dimer is composed of two fermions of very different masses the resulting exchange reaction should still be suppressed despite the overall bosonic nature. This could be accomplished by using fermionic ⁴⁰K and a long lived ⁸⁴Rb or ⁸⁶Rb. The comparison between reaction rates in the above described interactions can then be used to directly study the effects of fermion/boson spin statistics to that of chemical reactions.

5.3 Structure, energetics, and reactions of alkali tetramers^{*}

The successful trapping of both homonuclear and heteronuclear molecules in their ground rovibrational states reduces the probability of inelastic collisions but does not preclude the possibility of reactive collisions or association reactions. The thermochemistry of all homonuclear and heteronuclear diatomic alkali structures is now well documented [67]. In contrast, with the exception of Li₃, the structure and binding energies of higher alkali clusters are not well understood. Züchowski and Hutson [67] have explored the possibility of fragmentation reactions, such as $Na_2+Na_2 \rightarrow Na_3+Na$, and found that these $(2 + 2 \rightarrow 3 + 1)$ reactions are all endothermic and that trimer formation in ultracold traps is very unlikely. Byrd *et al.* [10] have recently carried out a detailed study of the structure of K_2Rb , KRb_2 and K_2Rb_2 . They find that trimer formation is strongly endothermic for both K_2+Rb_2 and KRb+KRb reactions, in agreement with the findings of Züchowski and Hutson [67]. The association reactions, $K_2+Rb_2 \rightarrow K_2Rb_2$ (C_s) and $KRb+KRb\rightarrow K_2Rb_2$ (D_{2h}), however, are found to be strongly exothermic with stable minima that are energetically very similar for both D_{2h} and C_s symmetries. The transition state connecting these two minima is found to be 1167 cm⁻¹ above the (D_{2h}) dissociation energy, indicating that both symmetries will be sampled for either association reaction.

The existence of higher clusters of alkali atoms has been reported in the adiabatic expansion of alkali vapors as early as the 1960s [165]. At room or elevated temperatures, alkali vapors are now known to contain small concentrations of molecular clusters ranging from double molecules, such as Na₄, to higher clusters containing as many as 100 atoms [166, 167]. Foster et al. [168] produced small clusters in Li, Na, K and C_s vapors and measured ionization potentials of both homopolar and heteropolar

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clusters ranging from Li₄ to Cs₄. Similar clusters formed in alkali vapors have been suggested by Ewing *et al.* [169] to explain experimental PVT data. Robbins, *et al.* [170], in adiabatic beam expansion studies of Na vapor, give ionization potentials of Na clusters containing up to eight atoms. Multiphoton dissociation, excitation, and ionization processes in Na_mK_n clusters are reported by Bartelt, *et al.* [171].

The ground states of homogeneous alkali clusters have been studied using a variety of quantum computational models [172–176]. In contrast, very few studies of the geometry and electronic structure of heterogeneous alkali clusters have been reported. Dahlseid *et al.* [143] have calculated the ground state properties and excitation energies of $Li_x Na_{4-x}$ clusters. They report HF/6-31G(d) geometries and energies, and single energy MP2 results at optimized HF geometries. One stable planar (C_s) structure and two stable rhombic (D_{2h}) structures were found for the tetramer Li₂Na₂. Jiang *et al.* [144] investigated Li_2Na_2 and Li_2K_2 structures as part of a more general study of neutral and ionic $Li_n Na_m$ and $Li_n K_m$ clusters. Their geometry optimizations were performed at the B3LYP/6-31G(d) level and refined at the B3LYP/6-311G(d)level. They find one stable rhombic (D_{2h}) structure for Li₂Na₂ and Li₂K₂ but do not find a second D_{2h} structure or the planar (C_s) structures reported by Dahlseid *et al.* [143]. Their structure for Li_2K_2 actually corresponds to the higher energy D_{2h} state with the K atoms located on the long diagonal. Bonačić-Koutecký et al. [177] have carried out the most complete study of Li₂Na₂ to date. They performed complete active space self-consistent field (CASSCF-CI) calculations with the (13s3p1d/6s3p1d) basis set for Li and the (12s8p1d/7s4p1d) basis set for Na, based on geometry optimization at the CASSCF level with the 3-21G basis set. Correlation effects were examined at the full CI (valence electrons), MRSD-CI, and MRD-CI methods in order to check whether there was an effect on the energy ordering of the several conformers of Li₂Na₂. They report two stable D_{2h} conformers, a stable C_s structure, and

Tetramer	R11	R22	R12	Erel (cm^{-1})
$Li_2(1)Li_2(2)$ I	2.689	5.446	3.037	0.
$Li_2(1)Li_2(2)$ TS	4.171	4.171	2.960	4721.8
$Li_2(1)Na_2(2) I$	2.720	5.923	3.259	0.0
$Li_2(1)Na_2(2)$ II	5.852	3.143	3.321	1738.7
$Li_2(1)Na_2(2)$ TS	4.381	4.748	3.230	5218.5
$Li_2(1)K_2(2)$ I	6.336	4.096	3.772	0.0
$Li_2(1)K_2(2)$ II	2.734	7.067	3.789	1348.5
$Li_2(1)K_2(2)$ TS	3.857	6.413	3.742	4146.8
$Li_2(1)Rb_2(2) I$	6.479	4.453	3.931	0.0
$Li_2(1)Rb_2(2)$ II	2.733	7.427	3.957	1285.3
$Li_2(1)Rb_2(2)$ TS	3.735	6.882	3.915	3713.9
$Li_2(1)Cs_2(2)$ I	6.559	4.912	4.098	0.0
$Li_2(1)Cs_2(2)$ II	2.727	7.959	4.207	2786.6^{*}
$Na_2(1)Na_2(2) I$	6.259	3.156	3.505	0.0
$Na_2(1)Na_2(2)$ TS	4.774	4.774	3.375	4576.0
$Na_2(1)K_2(2)$ I	6.745	4.105	3.948	0.0
$Na_2(1)K_2(2)$ II	3.164	7.442	4.043	2643.8^{*}
$Na_2(1)Rb_2(2) I$	6.920	4.454	4.115	0.0
$Na_2(1)Rb_2(2)$ II	3.162	7.834	4.224	2501.2^{*}
$Na_2(1)Cs_2(2)$ I	6.997	4.923	4.277	0.0
$Na_2(1)Cs_2(2)$ II	3.148	8.372	4.472	3698.1^{*}
$K_2(1)K_2(2)$ I	7.994	4.116	4.496	0.0
$K_2(1)K_2(2)$ TS	6.148	6.148	4.347	3471.8
$K_2(1)Rb_2(2) I$	4.116	8.388	4.672	0.0
$K_2(1)Rb_2(2)$ II	8.209	4.462	4.672	29.3
$K_2(1)Rb_2(2)$ TS	6.866	5.972	4.550	2115.4
$K_2(1)Cs_2(2)$ I	8.304	4.945	4.832	0.0
$K_{2}(1)Cs_{2}(2)II$	4.086	8.939	4.914	1088.6^{*}
$Rb_2(1)Rb_2(2)$ I	8.613	4.458	4.849	0.0
$Rb_2(1)Rb_2(2)$ TS	6.625	6.625	4.685	3225.9
$Rb_2(1)Cs_2(2)$ I	8.726	4.947	5.016	0.0
$Rb_2(1)Cs_2(2)$ II	4.426	9.178	5.095	1009.5^{*}
$Cs_2(1)Cs_2(2)$ I	9.397	4.899	5.299	0.0
$Cs_2(1)Cs_2(2)$ TS	7.257	7.257	5.132	2920.9

Table 5.5. Calculated CCSD(T)/def2-TZVPP tetramer geometries with D_{2h} symmetry (units are in ang.).

Tetramer	R12	R23	R34	R14	ϕ_{123}	ϕ_{234}
Li ₁ Li ₂ Na ₃ Na ₄	3.031	3.341	3.466	3.291	54.82	118.36
$\mathrm{Li}_{1}\mathrm{Li}_{2}\mathrm{K}_{3}\mathrm{K}_{4}$	3.007	3.867	4.422	3.815	58.10	104.76
${\rm Li_1Li_2Rb_3Rb_4}$	2.988	4.075	4.742	3.994	58.34	100.70
$Li_1Li_2Cs_3Cs_4$	3.007	4.226	5.252	4.165	60.16	95.56
$\mathrm{Na_1Na_2K_3K_4}$	3.571	3.873	4.655	3.991	58.41	111.18
$Na_1Na_2Rb_3Rb_4$	3.455	4.228	4.819	4.180	57.73	107.46
$Na_1Na_2Cs_3Cs_4$	3.492	4.338	5.408	4.305	60.12	101.26
$K_1K_2Rb_3Rb_4$	4.503	4.673	4.861	4.653	55.61	120.98
$K_1K_2Cs_3Cs_4$	4.569	4.789	5.486	4.751	57.26	114.73
$Rb_1Rb_2Cs_3Cs_4$	4.985	4.915	5.579	4.874	56.40	118.47

Table 5.6. Calculated CCSD(T)/def2-TZVPP tetramer geometries with C_s symmetry (Units are in ang. and degrees).

the transition state coupling the two D_{2h} states. Antoine et al. [178] studied the static dipole polarizability of several small lithium-sodium clusters using both DFT and CISD methods. They report one stable D_{2h} structure for Li₂Na₂. Byrd *et al.* [10] report one stable D_{2h} structure, a stable C_s structure, and the transition state between these two structures for the tetramer K₂Rb₂.

In this section we report calculated energetics for all possible alkali association reactions of the type $X_2+X_2 \rightarrow X_2X_2$, $X_2+Y_2 \rightarrow X_2Y_2$ and $XY+XY \rightarrow X_2Y_2$. We show that stable tetramers are found in both D_{2h} and C_s symmetries for reaction pairs from Li2 to Cs2. For Li₂Na₂, Li₂K₂, Li₂Rb₂ and K₂Rb₂, in addition to a stable C_s structure, we find two stable D_{2h} structures corresponding to both the light atoms and heavy atoms located on the short diagonal of the rhombus. The transition state (TS) connecting the two stable D_{2h} conformers has also been found.

Electronic structure calculations were performed for tetramers formed from all homopolar dimers ranging from Li_2 to Cs_2 and all heteropolar dimers ranging from LiNa to RbCs. Optimized geometries were found at the CCSD(T) level of theory [96, 97] with the Karlsruhe def2-TZVPP basis set [147]. The stability of these tetramers is mainly due to three-center bonds, as first described by Dahlseid *et al.* [143], and not primarily by correlation effects since these tetramer structures exhibit stability at the HF level of theory. Calculations carried out using DFT methods also indicate stability but with less accurate geometry and thermochemistry since double excitations are important. The CCSD(T) level of correlation was chosen based on previous studies by our group on alkali molecules. Harmonic vibrational frequencies were calculated to insure that we had located stable geometric minima. For Li, we chose to correlate all electrons; for Na and K, we correlated the valence and next inner shell electrons. For the systems containing Rb or Cs, we replaced the inner valence electrons of these atoms with the Stuttgart small-core relativistic effective core potentials [146]. Calculations optimized at the CCSD(T) level of theory with the Karlsruhe def2-QZVPP basis set [84] are reported by Byrd *et al.* [10] for the K_2Rb_2 tetramer. These larger basis set calculations show only small corrections in the optimized bond lengths and tetramer formation energies from the results reported here. However, they show that improved thermochemistry is found from single point energy calculations using the CCSD(T)-F12b [110, 111] explicitly correlated level of theory. All calculations were performed with the GAUSSIAN 09 [153], MOLPRO 2010.1 [123] and CFOUR [179] electronic structure packages.

Stable tetramer structures were found for both ${}^{1}A'(C_{s})$ and ${}^{1}A_{g}(D_{2h})$ electronic states for all molecular tetramers from Li₄ to Cs₄. We find that stable structures with D_{2h} symmetry can form from X₂+X₂ or XY+XY reactant pairs. Stable structures with C_{s} symmetry can form from either X₂+Y₂ or XY + XY reactant pairs. A large barrier, which arises from the high rearrangement energy required to form a heteronuclear bond, exists between X₂+Y₂ reactants and the formation of a stable tetramer with D_{2h} symmetry. However, the energetically allowed reaction path with C_{s} symmetry for X₂+Y₂ reactant pairs results in a tetramer that is energetically similar to a D_{2h} structure. Byrd *et al.* [10] have shown that there is a weak barrier

Reaction	$\rm kcal/mol$	cm^{-1}
$LiNa+LiNa\rightarrow Li_2Na_2 I$	16.41	5740.0
$LiNa+LiNa \rightarrow Li_2Na_2 II$	11.44	4001.3
$LiK+LiK\rightarrow Li_2K_2$ I	14.56	5090.8
$LiK+LiK\rightarrow Li_2K_2$ II	10.70	3742.3
$LiRb+LiRb\rightarrow Li_2Rb_2$ I	13.17	4605.6
$LiRb+LiRb\rightarrow Li_2Rb_2$ II	9.68	3386.2
$LiCs+LiCs\rightarrow Li_2Cs_2$	15.24	5328.6
$NaK+NaK \rightarrow Na_2K_2$	12.58	4399.0
$NaRb+NaRb\rightarrow Na_2Rb_2$	11.11	3887.1
$NaCs+NaCs\rightarrow Na_2Cs_2$	12.98	4540.8
$KRb+KRb\rightarrow K_2Rb_2 I$	7.44	2602.5
$KRb+KRb\rightarrow K_2Rb_2$ II	7.36	2573.2
$KCs+KCs\rightarrow K_2Cs_2$	8.61	3010.0
$RbCs+RbCs\rightarrow Rb_2Cs_2$	7.55	2640.6
$Li_2+Li_2\rightarrow Li_2Li_2$	17.96	6282.5
$Na_2+Na2\rightarrow Na_2Na_2$	9.78	3420.0
$K_2+K2\rightarrow K_2K_2$	8.53	2984.4
$Rb_2 + Rb2 \rightarrow Rb_2 Rb_2$	6.50	2274.6
$Cs_2+Cs2\rightarrow Cs_2Cs_2$	5.68	1985.2

Table 5.7. Reaction Energies for Alkali Tetramer Formation with D_{2h} symmetry. See Table 5.5 for the difference between I and II geometries.

between the K_2Rb_2 tetramers with C_s or D_{2h} symmetry. Thus both symmetries will most likely be sampled for either association reaction.

The significant question, for ultralow temperature collisions of these reactant pairs, is whether a long range barrier exists that would prevent reactants from forming stable tetramer structures. A model for describing long range interactions in alkali diatom pairs was recently reported [3]. This model included dipole-dipole (C_3) terms, quadrupole-quadrupole (C_5) terms and both dispersion and dipole induction energy (C6) terms. Stone [70] has shown that the C_3 and C_5 terms can exhibit either attractive or repulsive long range behavior, depending on the orientation of the colliding pairs. This suggests that a barrier-less path should exist for randomly oriented collisions. Byrd *et al.* [10] have examined this possibility by carrying out calculations for K₂+Rb₂ and KRb+KRb, at large diatom separations, as a function of reactant orientations. They find a reaction path that is barrier-less for the formation of a

Reaction	$\rm kcal/mol$	cm^{-1}
$Li_2+Na_2 \rightarrow Li_2Na_2$	13.23	4627.0
$LiNa+LiNa \rightarrow Li_2Na_2$	14.01	4901.2
${\rm Li}_2 {+} {\rm K}_2 ightarrow {\rm Li}_2 {\rm K}_2$	11.83	4136.5
$LiK+LiK \rightarrow Li_2K_2$	12.95	4530.1
${\rm Li}_2 + {\rm Rb}_2 \rightarrow {\rm Li}_2 {\rm Rb}_2$	10.45	3653.9
$LiRb+LiRb \rightarrow Li_2Rb_2$	11.94	4175.0
$\rm Li_2 + Cs_2 \rightarrow \rm Li_2 Cs_2$	11.23	3928.8
$LiCs+LiCs \rightarrow Li_2Cs_2$	11.48	4016.9
$Na_2+K_2 \rightarrow Na_2K_2$	9.25	3236.2
$NaK+NaK \rightarrow Na_2K_2$	8.90	3112.9
$Na_2+Rb_2 \rightarrow Na_2Rb_2$	7.92	2770.0
$NaRb+NaRb \rightarrow Na_2Rb_2$	7.81	2731.6
$Na_2 + Cs_2 \rightarrow Na_2Cs_2$	8.62	3013.9
$NaCs+NaCs \rightarrow Na_2Cs_2$	7.75	2710.2
$K_2 + Rb_2 \rightarrow K_2 Rb_2$	7.54	2637.4
$KRb+KRb \rightarrow K_2Rb_2$	7.42	2593.5
$K_2 + Cs_2 \rightarrow K_2 Cs_2$	7.82	2735.2
$\mathrm{KCs} + \mathrm{KCs} \rightarrow \mathrm{K}_2\mathrm{Cs}_2$	6.92	2421.6
$Rb_2{+}Cs_2 \rightarrow Rb_2Cs_2$	6.91	2416.4

Table 5.8. Reaction Energies for Alkali Tetramer Formation with C_s symmetry.

tetramer with either reactant pair. Similar findings were reported by Tscherbul [109] for the RbCs+RbCs reactant pairs and by de Miranda *et al.* [38] for KRb+KRb reactant pairs.

The CCSD(T)/def2-TZVPP geometries are tabulated in Table 5.5 for the stable D_{2h} structures and in Table 5.6 for the C_s structures. In general, the surfaces with D_{2h} symmetry are very flat. We find two stable D_{2h} structures for the tetramers Li_2Na_2 , Li_2K_2 , Li_2Rb_2 and K_2Rb_2 that are close in energy. For these four tetramers, a stable D_{2h} structure is found for both the case where the heavy atoms exhibit a short separation and the case where the light atoms exhibit a short separation. The relative energies of these two conformers are given in Table 5.5. For the tetramers, Li_2K_2 and Li_2Rb_2 , the more stable structure exhibits short heavy atom separation. For the tetramers, Li_2Na_2 and K_2Rb_2 , the more stable structure exhibits long heavy atom separation. The transition state structure for these four tetramers requires a
multi-reference treatment of the valence electrons since different orbital occupancies are found for the two possible D_{2h} structures. There are two degenerate D_{2h} structures for the tetramers Li₂Li₂, Na₂Na₂, K₂K₂, Rb₂Rb₂ and Cs₂Cs₂. These could be differentiated by isotope substitution on one diatom.

Our results for Li₂Na₂ are in agreement with the MP2/RHF calculations reported by Dahlseid *et al.* [143] who found both of the stable D_{2h} structures and a stable C_s structure. Their optimum geometries are somewhat extended compared with the results in this work since their optimization was carried out at the SCF level. A second complete study of Li₂Na₂ is reported by Bonačić-Koutecký *et al.* [176] who also located the transition state connecting the two stable D_{2h} structures. They report energies obtained from a full CI treatment for the valence electrons that are in good agreement with the CCSD(T) results reported here.

Reaction energies for the tetramer association reactions are given in Table 5.7 for structures with D_{2h} symmetry and in Table 5.8 for reactions resulting in tetramers with C_s symmetry. Reaction energies are defined as the total electronic energy for the tetramer minus the total electronic energies of the reacting dimer structures. Zero-point energy corrections are not included since they are small for these alkali structures and partially cancel in the calculated reaction energies. In general, the tetramers formed from the lighter alkalis exhibit larger association energies than those formed from the heavier alkalis. Comparing reaction energies for tetramers with C_s symmetry, reactions of the type $X_2+Y_2 \rightarrow X_2Y_2$ are more exothermic than reactions of the type $XY+XY\rightarrow X_2Y_2$, with the exception of tetramers formed from diatoms that contain Li. For the tetramers, Li₂Na₂, Li₂Kb₂, Li₂Rb₂ and K₂Rb₂, the C_s structure formed from heteropolar reactants lies energetically between the two stable D_{2h} structures. Of particular interest is formation of the K₂Rb₂ tetramer, where all reaction paths appear to be energetically similar. At low temperatures, direct formation of tetramers is unlikely, owing to the large exothermicity associated with these association reactions, but atom exchange reactions $(X_2+Y_2 \rightarrow XY+XY)$ are possible for species where the reaction energy is similar in either direction.

Other groups of alkali tetramers, based on the $X_2+XY \rightarrow X_3Y$ diatom reaction pair and the $X_2Y+X \rightarrow X_3Y$ atom-radical reactions, are possible. This first group of reactions has been previously reported for the formation of Li₃Na [143, 144, 178], for the formation of LiNa₃ [143, 144, 177, 178], and for the formation of Li₃K and LiK₃ [144]. In general, this group of tetramers exhibits C_v symmetry with two stable structures corresponding to both acute and obtuse X₃ angles. Calculated reaction energies are similar to those reported here for diatom-diatom association reactions. Reactions of the free radical type, X₂Y+X \rightarrow X₃Y, would be more energetic but are difficult to study experimentally.

5.4 Rubidium hydroxide associative detachment

Advances in the formation of cold molecules have opened up avenues into many branches of the physical sciences [14, 180]. For chemical physics, applications range from precision spectroscopy [46], to the study [26, 38] and control [50] of cold chemical reactions. Other areas of physics benefit greatly from the study of cold molecules, such as condensed matter physics [51], and the search for novel quantum gases [53] and phases [54]. Molecular ions have the further advantage of being easily trapped and cooled using radio frequency traps and sympathetic cooling [181]. The recent experimental work of Deiglmayr *et al.* [4] has co-trapped cold rubidium with hydroxide and investigated the associated reactive collisional processes. Their measured ion loss rate of 2×10^{-10} cm³s⁻¹ was found to be significantly smaller than the estimated Langevin ion capture rate of 4.3×10^{-9} cm³s⁻¹, but much larger than any expected quenching rate. The goal of this study is to identify the associative detachment process(es) that lead to the unexpectedly low measured reaction rate.

Electronic structure calculations were performed on RbH, RbO, OH, RbOH and associated anions using a combination of perturbation and coupled cluster theory [97]. Second order Møller-Plesset (MP2) perturbation theory and coupled cluster theory with all singles, doubles, and perturbative triples (CCSD(T)) energy and gradient calculations in this work were carried out using the CFOUR [179] and MOLPRO 2010.1 [182] quantum chemistry packages. Higher order calculations involving CCSDT and CCSDT(Q) (all triples and perturbative quadruples respectively [183]) were done using the MRCC program of M. Kállay [184]. For open shell systems, the spin restricted variants of these theories were used. Due to the size of rubidium, there are a number of correlation space choices available for consideration. We have adopted the same notation as Sullivan *et al.* [185] where valence only calculations (H:1s; O:2s2p; Rb:5s) are referred to as relaxed valence (rv). Increasing the correlation space size to in-

	r(M-H)	r(M-O)	ZPE*[186]	EA	AE
OH	0.9698		8.53		162.91
Exp.	0.9696[187]		8.51[186]		161.53[188]
OH^-	0.9643		8.55	1.8405	176.51
Exp.	0.9643[189]		8.51[189]	1.8277[190]	175.65[191]
RbO		2.3548	0.79		102.21
Exp.		2.2541[192]	0.84[192]		
$\rm RbO^-$		2.2564	0.65	0.1002	58.90
RbH	2.3919		1.12		61.39
Exp.	2.37[193]		1.34[193]		
RbH ⁻	2.5415		1.66	0.3604	47.11
RbOH	0.9551	2.3408	11.72		291.26
Theory	0.959[194]	2.472[194]	11.36[194]		
RbOH ⁻	0.9567	2.4166	11.27	0.2912	247.98

Table 5.9. Computed bond lengths, harmonic zero point energies, electron affinities (EA) and atomization energies (AE) for RbOH, its constitutes and their anions (Units are in angstroms, electron volts and 10^{-3} a.u. as appropriate).

volve the first set of sub-valence orbitals (H:1s; O:1s2s2p; Rb:4s4p5s) results in the relaxed inner-valence (riv), while spaces including yet deeper orbitals (H:1s; O:1s2s2p; Rb:3s3p3d4s4p5s) are called riiv and so forth. Valence (rv) only calculations involving rubidium and oxygen require extra care, as the usual method of energy sorting orbitals in selecting the frozen core will fail since the energy of 2s orbital of oxygen is below the 4p orbital of rubidium. Failing to properly choose the core orbitals for valence calculations will lead to significant errors.

While there are many basis sets available for the first row elements, the basis set selection for rubidium is sparse. This is further complicated by the need for diffuse functions to accurately describe electron affinities [195]. Previous calculations [10, 11] involving rubidium using the Karlshruhe def2-nZVPP basis sets [84, 147] (n=T,Q zeta quality basis sets with two extra *spdf* correlation polarization functions) have shown good experimental agreement for both dissociation energies and bond lengths of the Rb₂ diatom. For rubidium these basis sets use the small-core ECP28MWB [85] Stuttgart pseudopotential, which removes the argon core electrons from the calculation while leaving the 4s4p5s electrons free for use in further correlation calculations. The addition of even tempered *spdf* diffuse functions to these basis sets was done to better describe the anion, while the addition of these diffuse functions has also shown to improve molecular properties [5, 87] as well. This aug-Def2-nZVPP basis set was used for rubidium in all electronic structure calculations in this work. To best describe the OH bond, the optimized aug-cc-pVnZ valence [195] and aug-cc-wCVnZ weighted core-valence [196] correlation basis sets were used for hydrogen and oxygen respectively.

Molecular structures were optimized using the CCSD(T)/riv level of theory using the quadruple zeta (QZ) quality basis sets *. Frequency calculations at the riv CCSD(T) level of theory using the QZ basis sets were performed for each optimized structure to identify whether the structure was a transition state or a local minimum of the potential energy surface. The final ground state structure of the RbOH⁻ ion is found to be linear, consistent with the ground state structure of the neutral molecule [194, 197]. Additionally the conformers $OHRb^-$ and $ORbH^-$ were also investigated and found to be transition states. Vibrational harmonic zero-point energy (ZPE) corrections were computed for the final structures at the CCSD(T)/riv level of theory using the QZ basis set. Computed bond lengths and ZPE corrections are listed in Table 5.9.

Calculations involving the riiv electrons of rubidium require special care, as relativistic and core correlation effects are strong. The Roos atomic natural orbital (ANO) basis set [198] was chosen for its availability for all atoms present and its noted consistency. Before use the basis set was completely uncontracted so as to be as flexible as possible in subsequent correlation calculations. Scalar relativistic effects

^{*}It should be noted that bond lengths computed using MP2 theory differ only by a few mÅ from CCSD(T) calculations using the same basis set, at a much cheaper computational cost

method	space	Rb+OH ⁻	Rb+OH
CCSD(T)/TZ	riv	75.40	129.25
CCSD(T)/QZ	riv	74.63	130.47
CCSD(T)/Extrap.	riv	74.07	131.36
$\Delta CCSD(T)/ANO$	riiv	0.25	0.21
Total Energy	-	74.20	131.54

Table 5.10. Breakdown of the contributions of various levels of theory to the Rb-O bond energy (in 10^{-3} a.u.) for both neutral and charged RbOH.

were accounted for by adding in the one-electron second-order Douglas-Kroll-Hess [107, 108] contribution. For rv and riv calculations, which use the Def2 basis sets for rubidium, the small core MWB and MDF family of pseudopotentials have been shown [85, 146] to accurately account for the relativistic contributions to the bond length and dissociation energy.

The complete basis set limit (CBS) of the various contributions to the total energy was estimated using the two point linear extrapolation formula of Helgaker *et al.* [152],

$$E_{\text{CBS}}(\text{method}) = \frac{n^3 E_n - (n-1)^3 E_{n-1}}{n^3 - (n-1)^3}.$$
(5.17)

This extrapolation scheme was chosen over other more optimized schemes due to the spread of basis sets and correlation spaces used here. The final interaction energy is computed from the various contributions by the following formula

$$E_{\text{int}} = E_{\text{CBS}}(\text{CCSD}(\text{T})/\text{riv}) + E(\Delta \text{CCSD}(\text{T})/\text{riiv}), \quad (5.18)$$

where E(CCSD(T)/riv) is the total CCSD(T)/riv energy and

$$E(\Delta CCSD(T)/riiv) =$$
$$E(CCSD(T)/ANO/riiv) - E(CCSD(T)/ANO/riv) \quad (5.19)$$



Figure 5.9. Dissociation limits of rubidium hydroxyl (left) and its anion (right) up to the atomization limit. Energies are computed at the CCSD(T)/CBS level of theory.

is the riiv contribution. Higher order triples contributions beyond the CCSD(T) level of theory were estimated by performing CCSDT/rv calculations using QZ quality basis sets. Effects of connected quadruple excitations, known [191] to be important for OH⁻, were estimated using CCSDT(Q)/rb with the TZ quality basis sets. It was found that the contribution of these higher order terms to the final EA are small (< $.05 \times 10^{-3}$ a.u.) due to cancellation. While the riiv correlation contribution is similarly small for the EA of RbOH at the equilibrium geometry, it becomes more significant for much shorter Rb-O bond lengths (further discussed below). In Table 5.10, the contributions of each of these corrections to the Rb-O bond energy are listed. Molecular bond lengths, electron affinities (EA) and atomization energies (AE) (including the harmonic ZPE correction) are reported in Table 5.9. The excellent agreement with available experimental bond lengths, harmonic frequencies and electron affinities leads us to expect comparable accuracy for the RbOH complex.

The EA and similar geometric structure of rubidium hydroxyl and its anion, along with the large difference in neutral and anion dissociation limits illustrated in Fig. 5.9, does not suggest immediately a charge loss pathway. In fact, at 300 Kelvin no other dissociation channels are energetically accessible. This is clearly illustrated in Fig. 5.10 where the minimum energy dissociation path of Rb for both RbOH and its anion are computed at the fixed OH bond CCSD(T)/riv/CBS level of theory. It can be seen that the neutral and anion curves do not cross at any point along the incoming path. However it should be noticed that the inner wall of these curves become nearly degenerate at this level of theory. We examine the inner wall more closely, by relaxing the OH bond at each Rb-O distance using MP2 gradients (as noted previously, MP2 bond lengths are very close to CCSD(T) bond lengths), and find that indeed the neutral and anion curves cross at r(Rb-O) \sim 1.81Å $\,$ with a barrier height of $V_c(0) \sim 30.0 \ 10^{-3}$ a.u. above the Rb+OH⁻ dissociation limit, as illustrated in Fig. 5.11. This crossing energy $V_c(\theta)$ also includes the CCSD(T)/riiv correction which provides $\sim 0.4 \ 10^{-3}$ a.u. to the final barrier height. This crossing is energetically accessible if the internal rotational and vibrational energy of OH⁻ is taken into account. In fact, it is well known that producing rotationally and vibrationally cool OH^- is difficult experimentally [189].

The height of $V_c(\theta)$ for geometries other than the linearly minimum energy approach was also investigated. It was found that for small angle approaches, relative to the equilibrium geometry, the crossing remains relatively flat, while for angles greater



Figure 5.10. Potential energy curve of Rb+OH and its anion computed along the $C_{\infty v}$ axis at the CCSD(T)/CBS level of theory. The OH bond length is held fixed over the entire curve for simplicity. Also shown are the energy asymptotes for various OH⁻ vibrational levels.

than 40 degrees the barrier rapidly increases in height until it is completely energetically inaccessible (see Fig. 5.11). We estimate then the effective angular phase space where the curve crossing is accessible to be

$$\rho_c(E_T, \theta) = \frac{1}{4\pi} \Theta(E_T - V_c(\theta) + \Gamma(v, J))$$
(5.20)

where $\Theta(\dots)$ is a Heaviside step function representing the height of the crossing as a function of the collisional angle, $\Gamma(v, J)$ accounts for any internal motion of the complex and E_T is the collision energy. The total ion capture cross-section can then be computed by combining the accessible angular space $\rho_c(E_T, \theta)$ and the Langevin ion capture cross-section [199]

$$\sigma_L(E_T) = \pi \left(\frac{2\alpha}{E_T}\right)^{1/2} \tag{5.21}$$

as

$$\sigma_{\text{total}}(E_T) = 2\pi\sigma_L(E_T)\rho_c(E_T,\theta)$$
(5.22)

where we have integrated over the azimuthal angular dependence. Here α is the polarizability of the neutral monomer, k_b is the Boltzmann constant and it is assumed that the reaction probability at the curve crossing is 1.

The thermal rate constant k_L is given in terms of the total cross-section as

$$k_L = \left(\frac{8}{\pi\mu\beta}\right)^{1/2} \int_0^\infty d\left(\beta E_T\right) \left(\beta E_T\right) \exp\left(-\beta E_T\right) \sigma_{\text{total}}(E_T)$$
(5.23)

where $\beta = 1/k_b T$ and T is the translational temperature. Inserting Eq.(5.22, substituting $b = \beta E_T$ and integrating over the remaining angular dependence we obtain

$$k_L(v,J) = \left(\frac{2}{\pi\mu\beta}\right)^{1/2} \int_0^\infty d(b)(b) \exp(-b)\sigma_L(\beta b)$$
$$\times \int_0^\pi d\theta \Theta((\beta b - V_c(\theta) + \Gamma(v,J))/\beta) \sin\theta \quad (5.24)$$

where then $\Gamma(v, J) = T(v, J)$ is the internal rotation-vibration energy the OH⁻ fragment $T(v, J) = G(v) + F_v(J)$, of the v'th vibrational and J'th rotational state, which we take to follow a Dunham series [200]. The distribution of rotational states is assumed to be thermal, but with a temperature $T_{\rm rot}$ (e.g. the rotational energy is not



Figure 5.11. Inner wall potential energy curve of Rb+OH and its anion computed for various collisional angles at the CCSD(T)/CBS level of theory with the OH bond length relaxed at each point of the curve.

thermalized against the translational energy), which gives the vibrational state rate constant

$$k_L(v) = \frac{1}{Q_{\rm rot}} \sum_{J}^{J_{\rm max}} k_L(v, J) \exp\left(-\beta_{\rm rot} F_v(J)\right),$$
(5.25)

with the rotational partition function given by

$$Q_{\rm rot} = \sum_{J}^{J_{\rm max}} \exp\left(-\beta_{\rm rot} F_v(J)\right).$$
(5.26)

Here J_{max} is the maximum rotational state taken in the series. To evaluate Eq.(5.25) we use the spectroscopic constants of Rosenbaum *et al.* [189] in T(v, J) and choose J_{max} such that the thermodynamic contribution of that rotational state is negligible. A value of $J_{\text{max}} = 15$ was found to be more than adequate to converge the sums in Eqs.(5.25-5.26) even for very high rotational temperatures. The integral in Eq.(5.25) was evaluated numerically for the first three vibrational levels of OH⁻ as a function of the rotational temperature, the results of which are plotted in Fig. 5.12. The rate for v = 0 and v = 1 is found to be much lower than the experimental value, which is expected considering the energetics of the collision. However this is not the case for v = 2 where the computed rate is in excellent agreement with the experimental results. It should be noted that for v = 2 and higher, the incoming collisional energy is above the curve crossing threshold, and so is a nearly constant as expected.

From these results we expect a predominance of vibrationally excited OH^- molecules within the current experimental apparatus, thus leading to the observed loss rate to be larger than expected. With additional vibrational quenching this loss rate can be reduced significantly. This can be done by a longer exposure to the initial neon buffer gas or by a different choice in buffer gas such as helium (which provides a better reduced mass ratio). In reducing the reaction rate it should then be possible to much more efficiently sympathetically cool the trapped hyroxide. Also, due to the strong vibrational and orientational dependence of the reaction, it should be possible to probe the reaction process through vibrational state selection or by alignment of the OH^- molecule.



Figure 5.12. Ion capture rate constants as a function of the collisional temperature of the OH^- complex for the first three vibrational levels at various translational energies. Included is the experimental rate of Deiglmayr *et al.* [4].

Chapter 6 Summary and Outlook

In this work we have presented our formulation of the long range interaction between two arbitrary molecules in Section 2.2, with the special case of the interaction of two linear molecules worked out specifically in Section 2.1. With this formalism we have computed the long range interaction (electrostatic + induction + dispersion) coefficients for the X_2+X_2 and XY+XY alkali diatomic molecules from lithium to cesium, including all electrostatic moments and static polarizabilities through $\ell = 3$, using density functional and coupled cluster theory. In presenting the long range interaction between two general molecules, we have also derived in Section 2.3 the closed form expression for the long range interaction between rotationally dressed molecules as well as the analytic solution for rotational states generated by a low DC electric field (Section 2.4).

In Section 4.1 we apply the rotational state dressing formalism to the case of confined and aligned KRb molecules. We explore one-dimensional samples of ultracold polar molecules with attractive dipole-dipole interactions and show the existence of a repulsive barrier caused by a strong quadrupole interaction between molecules. This barrier can stabilize a gas of ultracold KRb molecules and even lead to long range wells supporting bound states between the molecules. The properties of these wells can be controlled by external electric fields, allowing the formation of long polymer like chains of KRb and studies of quantum phase transitions, by varying the effective interaction between molecules. In Section 4.2 we extend our evaluation of DC field

alignment from KRb to all other alkali heteorouclear molecules through Cs. From our results it is possible to estimate the ocurrance of a long range quadrupolar barrier through the evaluation of the long range parameter R_q (Eq.(4.5)).

In our study of alkali tetramer reaxtionst the lowest doublet electronic state for the lithium trimer $(1^2A')$ is calculated for use in three-body scattering calculations using the valence electron FCI method with atomic cores represented using an effective core potential. It is shown in Section 5.1 that an accurate description of core-valence correlation is necessary for accurate calculations of molecular bond lengths, frequencies and dissociation energies. Interpolation between $1^2A'$ *ab initio* surface data points in a sparse grid is done using the global interpolant moving least squares method with a smooth radial data cutoff function included in the fitting weights and bivariate polynomials as a basis set. The Jahn-Teller splitting of the $1^2E'$ surface into the 1^2A_1 and 1^2B_2 states is investigated using a combination of both CASSCF and FCI levels of theory. Additionally, preliminary calculations of the $1^2A''$ surface are also presented using second order spin restricted open-shell Møller-Plesset perturbation theory.

To understand possible reaction paths and molecular combinations requires accurate studies of the fragment and product energetics. To this end We have calculated in Section 5.2 and 5.3 accurate gradient optimized ground-state structures and zero-point corrected atomization energies for the trimers and tetramers formed by the reaction formed from $X_2+X_2 \rightarrow X_2X_2$, $X_2+Y_2 \rightarrow X_2Y_2$, and $XY+XY \rightarrow X_2Y_2$ alkali dimer association reactions. Vibrationally stable rhombic (D_{2h}) and planar (C_s) structures are found for all possible tetramers formed from the alkali metals, Li to Cs. All tetramer formation reactions (from ground state singlet homonuclear or heteronuclear dimers) are found to be exothermic with binding energies ranging from 6282 cm^{-1} for Li₂Li₂ to 1985 cm⁻¹ for Cs₂Cs₂. Extensive calculations, carried out at long range for several reactant pairs, indicate that there are barrier-less pathways for the formation of tetramers from dimer association reactions. At low temperatures, direct formation of tetramers is unlikely, owing to the large exothermicity associated with these association reactions, but atom exchange reactions $(X_2+Y_2 \rightarrow XY+XY)$ are possible for some species.

Finally, in Section 5.4 we present the recent work on understanding recent experimental ion loss rate results. Electronic structure calculations have been performed to compute the optimized structure, harmonic vibrational frequencies and dissociation energies of RbOH and its anion. The electron affinity of RbOH was computed to be 0.2890 eV, with an $Rb+OH^-$ bond energy half that of the neutral bond. To determine other possible charge loss pathways, the Rb+OH and $Rb+OH^-$ dissociation curves were computed using couple cluster methods along all possible collisional angles. An adiabatic curve crossing between the neutral and charged molecule was found at the inner wall of the molecular potential curve for linear geometries. Associative detachment rates were estimated using the Langevin ion capture cross-section. The inclusion of vibrationally excited vibrational states were found to be necessary to obtain agreement with current experimental reaction rates.

Appendix A

Anisotropic Long Range Molecular Interactions: Implementation

The purpose of this chapter is to provide an overview of the van der Waals program implementing the evaluation of Eq.(2.31) and associated molecular properties. It is expected that the reader will have the actual source code on hand, though it is not completely necessary. Also in section A.13 is the programmers file that is included with the source code. This file contains a summary of the internal routines, as well as the project makefile with associated comments.

A.1 Derived data types

The main van der Waals program is written using Fortran 90/2003, and the derived data typing available in the new Fortran was extensively used. A thorough discussion of derived data types in Fortran is well beyond the scope here, however the unfamiliar reader should keep in mind that Fortran derived data types are in the same family as object classes in C++.

In the *smsab* program there are three data classes used:

- monomer,
- clf,
- vdw.

The **monomer** data type contains the memory pointers for transition moment data, uncoupled tensor products, electrostatic moments (cartesian and spherical) and polarizabilities (cartesian and spherical). Each monomer's rotation expansion coefficients are stored in the **clf** derived data type (see Section 2.3 for the mathematical details). Lastly, the **vdw** data type holds the program logical variables, skeleton index matrix and van der Waals coefficient arrays.

A.2 Driver flow

This section discusses the overall program flow as runtime progresses through the driver routine, *driver.f90*//**program driver**. The structure of *smsab* is a branching system where all initiation commands come from the driver program. Input logic and file control is also initiated in the driver program. In this section each important code block of the driving routing will be briefly described.

The driver program initially declares the derived data types used in smsab, following generic includes and variable declarations. Here we see a monomer data type for molecule A and B (**monomer** and **clf**), with a sequence of vdw data types for each order n.

```
type(monomer) :: A,B
type(vdw) :: vv, vv3, vv4, vv5, vv6, vv7, vv8, vv1f
type(clf) :: lfA, lfB
```

This section handles initial input argument logic using the select case syntax. Each case sets the appropriate logical variables and calls the memory initialization routines (further discussed in Sec. A.4).

```
select case (trim(buffr))
case('-h')
write(iw,*) "__README_contents:"
call system("cat_README")
stop
case('-alpha')
case('-l')
case default
end select
```

Following the initial input control, extra logic is used to detect field coupling. All A-B calculations involve either two or three initial calling arguments, the logic at the top of the following code decides where to look.

```
! extra input?
tone = vv%islinr.and.cmndnum>3
ttwo = .not.vv%islinr.and.vv%vdwsms.and.cmndnum>2
if(tone.or.ttwo) then
select case(trim(buffr))
```

```
case ('-restart')
case ('-rc')
end select
end if
```

Clebsch-Gordan values are computed and stored in an array at run time. This provides noticeable speedups. At the time of this writing, the Clebsch-Gordan routines are computed twice (once for each monomer) for ease of programmer time.

```
call generateclebg(A)
call generateclebg(B)
```

Initialization of van der Waals coefficient arrays, order by order, are done here. The data type flag "vv3%skelindtype" is an integer flag used to decide memory allocation and skeleton matrix computation logic.

```
skelindtype = 13 \implies c3
1
!
         skelindtype = 14 \implies c4
!
         skelindtype = 15 \implies c5
!
         skelindtype = 2 \implies
                                 c6
!
         skelindtype = 3 \implies
                                c7
1
         skelindtype = 4 \implies c8
vv3%islinr = vv%islinr
vv3\%skelindtype = 13
vv3%skelname='C3'
call indskel(vv3)
if (vv%verbose) call printskel (vv3)
vv8%islinr = vv%islinr
vv8\%skelindtype = 4
vv8%skelname='C8'
call indskel(vv8)
```

The polarizability properties of each monomer are computed at every run time. Then the logic and calls for a restart calculation are processed. This logic decides between reading in saved van der Waals coefficients or computing them using the vdw.f90//electrostatic, vdw.f90//induction and vdw.f90//dispersion routines.

```
 \textbf{call polarizability} (A, vv) \\
```

```
call polarizability (B, vv)
```

```
if(vv%vdwread) then
write(iw,10)
call openfo(vv%ioo,vv%oname)
call readvdw(vv,vv3,vv4,vv5,vv6,vv7,vv8)
vv%fprnt = .false.
else
call electrostatic(A,B,vv,vv3,vv4,vv5)
call induction(A,B,vv,vv6,vv7,vv8)
call dispersion(A,B,vv,vv6,vv8)
vv%fprnt = .true.
end if
```

Print coefficients, possibly to disk in addition to STDOUT, using

sms.f90//**vdwcoefprint**.

```
if (vv%fprnt) then
call openfn(vv%ioo,vv%oname)
end if
call vdwcoefprint(A,B,vv,vv3,vv4,vv5,vv6,vv7,vv8)
```

If we only want to compute the dynamic polarizability of a monomer, then all van der Wals coefficient calculations (see above) are skipped and the polarizability code is called again, with an additional logical variable calling additional response code.

```
if(A%alphad) then
call polarizability(A,vv)
end if
```

Following all coefficient computation, a rotational coupling calculation can be performed. This is done via vdw.f90//rcouple, with a separate printing routine sms.f90//printrc. Using a preprocessor flag it is possible to turn on and print out the $\sqrt{(4\pi)}$ normalization between (2.43) and the corresponding equation in Byrd *et al.* [6]

```
if(vv%couplelf) then
vvlf%skelindtype = 500
call createvdwind(vvlf)
call rcouple(A,B,vv,vv3,vv4,vv5,vv6,vv7,vv8,vvlf,lfA,lfB)
call printrc(lfA,lfB,vvlf)
#ifdef iLLF
! sqrt(4*pi) scaling to compare against old results.
```

```
write(iw,*) "---"
write(iw,*) "...sqrt(4*pi)_legacy_scaling_factor"
vvlf%clfc3 = vvlf%clfc3*dsqrt(4.d0*pi)
vvlf%clfc4 = vvlf%clfc4*dsqrt(4.d0*pi)
vvlf%clfc5 = vvlf%clfc5*dsqrt(4.d0*pi)
vvlf%clfc6 = vvlf%clfc6*dsqrt(4.d0*pi)
vvlf%clfc7 = vvlf%clfc7*dsqrt(4.d0*pi)
vvlf%clfc8 = vvlf%clfc8*dsqrt(4.d0*pi)
call printrc(lfA,lfB,vvlf)
#endif
end if
```

The program ends with clearing all memory allocations.

call destroyvdwind(vv3)
.
.
call destroym(A)
.

A.3 Input of *ab initio* data

Monomer transition moment data files are to be structured as follows:

\$GENVDW	basic check for non-legacy input						
I10	n <number excited="" of="" states=""></number>						
3E24.14	dmx dmy dmz <dipole vector=""></dipole>						
9E24.14	qmxx qmxy qmxz qmxy qmyy qmyz qmxz qmyz qmzz &						
	<symmetric moment="" quadrupole="" tensor=""></symmetric>						
10E24.14	omxxx omxxy omxxz omxxy omyyy omyyz omxzz omyzz omzzz omxyz &						
	<symmetric moment="" octupole="" tensor=""></symmetric>						
20E24.14	EIGEV TX TY TZ TXX TXY TXZ TYY TYZ TZZ &						
TXXX TYYY TZZZ TXXY TXXZ TXYY TYYZ TXZZ TYZZ TXYZ $\&$							
	<excitation energy, transition moments continued n times $>$ ')						

A.4 Initialization and Memory control

Calls to *sms.f90*//**initiate**(A) will open the monomer A transition moment data file, allocate the memory for monomer A and populate the coupled transition moment tensors.

```
subroutine initiate(A)
    implicit none
    include "io.h"
    type(monomer) :: A
! open the file
    call openfo(A%io,A%fname)
! read moments file and internally produce spherical moments
    call readtm(A)
    return
```

Memory allocation (deallocation) is handled in the following routines:

- *sms.f90*//**createm** (*sms.f90*//**destroym**),
- *sms.f90*//**createvdwind** (*sms.f90*//**destroyvdwind**),
- *sms.f90*//**createlf** (*sms.f90*//**destroylf**).

The first allocates memory for the **monomer** data type, the second allocates memory for the **vdw** data type. As we do the coefficient computation order by order, there is a subsequent logic for allocating only the order requested within sms.f90//createvdwind, the integer flag controlling this being "%skelindtype." Finally the third routine handles the rotational coupling expantion arrays. Within each memory allocation routine the arrays are initialized to 0.

A.5 Construction of initial tensors

Transition moments, from dipole to octupole, are computed *ab initio* in cartesians. So a conversion to spherical moments is required at some point within the code. Previous versions performed the conversion in the *ab initio* code, while the original program hard coded the spherical coefficients in terms of cartesians. For the most flexibility in *ab initio* program choice and within the van der Waals code itself, we read in the moments in cartesians and convert to spherical at the same time. The coupled transition moment tensor given by Eq.(2.25) is needed for computation of the van der Waals coefficients. To construct Eq.(2.25), we first compute the spherical transformation of each cartesian moment by a look up table (see Edmonds [73] for a printed table) and store in a temporary two index array ($T_{\ell m}$) as illustrated here.

 $\frac{! \, dip \, ole \ transition \ tensor}{\mathrm{Tt}(1,-1) = (\mathrm{TDx}-\mathrm{ai}*\mathrm{TDy})/\,\mathrm{dsqrt}(2.\,\mathrm{d0})}{\mathrm{Tt}(1,0) = \mathrm{TDz}} \\ \mathrm{Tt}(1,1) = -(\mathrm{TDx}+\mathrm{ai}*\mathrm{TDy})/\,\mathrm{dsqrt}(2.\,\mathrm{d0}) \\ \frac{! \, quadrup \, ole \ transition \ tensor}{\mathrm{Tt}(2,-2) = \mathrm{dsqrt}(3.\,\mathrm{d0}/2.\,\mathrm{d0})*(\mathrm{TQxx}-2.\,\mathrm{d0}*\mathrm{ai}*\mathrm{TQxy}-\mathrm{TQyy})/2.\,\mathrm{d0}} \\ \frac{.}{\mathrm{Tt}(2,0) = (-\mathrm{TQxx}-\mathrm{TQyy}+2.\,\mathrm{d0}*\mathrm{TQzz})/2.\,\mathrm{d0}} \\ \frac{.}{\mathrm{Ctup ole \ transition \ tensor}}{\mathrm{Tt}(3,-3) = \mathrm{dsqrt}(5.\,\mathrm{d0})*(\mathrm{TOXXX}-3.\,\mathrm{d0}*\mathrm{ai}*\mathrm{TOXXY}-3.\,\mathrm{d0}*\mathrm{TOXYY}+\mathrm{ai}*\mathrm{TOYYY})/4.\,\mathrm{d0}} \\ \frac{.}{\mathrm{Ctup ole \ transition \ tensor}}{\mathrm{Tt}(3,0) = (-3.\,\mathrm{d0}*\mathrm{TOXXZ}-3.\,\mathrm{d0}*\mathrm{TOYYZ}+2.\,\mathrm{d0}*\mathrm{TOZZZ})/2.\,\mathrm{d0}}$

As it is the product between transition moments that is needed, we store the uncoupled tensor product of each transition moment as a three index array $(T_{kmm'}, k \text{ is the}$ index over excited states) in the **monomer** data class.

$$A\% tensMN(i, ia, ib) = Tt(\ell, m) \times Tt(\ell', m').$$
(A.1)

Where M, N = D, Q, O for $\ell, \ell' = 1, 2, 3$ respectively. This means we store a separate array for each tensor product, order by order (DD, DQ, DO, QQ, QO, OO).

The analogous process is performed for the electrostatic moments in mlib.f90//Qtlookup, the difference being the obvious lack of a k index over excited states. The naming convention and other related aspects remain consistent with the transition moment routines/arrays.

A.6 Construction of skeleton indices

At the time of this writing, the skeleton index ({ Λ } from section 2.2) is computed via a hard coded set of routines in *mlib.f90*//**indskel**. In this routine the { Λ } indices are iterated over and stored in five arrays, where each element is iterated over the total space order ($\mathcal{O}(R^{-n})$) by order^{*}. The basic structure of the code is written in an extremely vectorizable way (in a compiler sense), meaning that loops are extracted and flattened out in blocks over *L*. This has the advantage of allowing explicit control over each block, with the downside being difficulty in including higher symmetry in a natural way. As the code is intended for the general no symmetry case, this is not seen as a serious downside.

The desired order is requested in *mlib.f90*//**indskel** by the integer flag "skelind-type" as:

- skelindtype = $13 \rightarrow C_3$
- skelindtype = $14 \rightarrow C_4$
- skelindtype = $15 \rightarrow C_5$
- skelindtype = $2 \rightarrow C_6$
- skelindtype = $3 \rightarrow C_7$
- skelindtype = $4 \rightarrow C_8$

^{*}As a special case the linear molecule is also hard coded and can be selected via input flags.

A.7 Monomer properties: polarizability

The computation of the uncoupled^{*} polarizability given by Eq.(2.32) is done in vdw.f90//cartAw and vdw.f90//spherAw for each given monomer, the results of which are store in the **monomer** data class. As the transition moment tensors of Eq.(A.1) are formed from tensor products but not coupled, Eq.(2.32) is trivially evaluated by the obvious summation over excited states and loops over m indices. If requested, the dynamic uncoupled polarizability of Eq.(2.33) is also computed on a Gauss-Chebyshev grid and printed to STDOUT[†].

Additionally the $S_k(0)$ metric Eq.(2.34) is evaluated for each monomer as a function of excited state, k, and printed to disk.

^{*}and cartesian for the dipole polarizability.

[†]Note that the dynamic polarizability is printed in cartesians only

A.8 Comment on restarts

On standard runs, the final van der Waals coefficients are printed to disk in the sms.f90//vdwcoefprint routine. The legend for the output file is

'N '	$^{\prime}L1$ $^{\prime}$	'K1 '	$^{\prime}L2$ $^{\prime}$	'K2'	'L '	'real_part'	'complex_part'
------	---------------------------	-------	---------------------------	------	------	-------------	----------------

using the format below.

FORMAT(2X, I1, 2X, I1, 1X, I2, 2X, I1, 1X, I2, 2X, I1, 3X, 2E24.14)

It is then possible to run restart jobs, in the sense that you can read in previously computed coefficients and a) print them out again to STDOUT with all the associated information and b) run further computation such as field coupling (see section 2.3). The restart itself is done via the *io.f90*//**readvdw** routine and is a sequence of loops working through the various **vdw** data type pointers.

A.9 Evaluation of $W_{n\{\Lambda\}}^{(1)}$

Having computed the electrostatic moments on read in (see section A.5), the construction of the electrostatic interaction coefficients $W_{n\{\Lambda\}}^{(1)}$ given by 2.22 is a simple set of loops over the $\{\Lambda\}$ skeleton indices. This is done in the vdw.f90//electrostatic routine. A sample loop is given below.

A.10 Tensor contraction/coupling

The tensor contraction/coupling of the transition moments given in Eq.(2.25) has to be computed for all { Λ } indices. As the transition moment tensors are stored in named arrays as described in Eq.(A.1), the contraction routines are also individually named for each order (example: *mlib.f90*//**tcont11** for the *DD* term). The idea here is effort of the part of the programmer will lead to longer but simpler code for the compiler to use. The loops themselves are simple after logic switches through the stored Clebsch-Gordan arrays. As many transition moments are small, thresholding is performed for a modest speedup in runtime. It should be pointed out that the computation of the Clebsch-Gordan routines on the fly in this routine more than doubles the runtime of the program. This should be an unsurprising result as many of these Clebsch-Gordan coefficients are called more than once for the same set of indices.

```
function tcont11(A,L,M, istate) result(tprod)
use sms
implicit none
include "ctcont.h"
include "io.h"
include "thresh.h"
integer, parameter :: l1=1, l2=1
t prod = (0.d0, 0.d0)
if(L==0.and.M==0) then
  do m1 = -11, 11
   do m2 = -12, 12
     if (abs(A%tensDD(istate,m1,m2)) < thresh) cycle
     if(m1+m2=m) tprod = tprod + &
                  A\%tensDD(istate,m1,m2)*A\%clebg110(m1,m2,M)
   end do !m2
  end do !m1
else if (L==2) then
```

A.11 Evaluation of $W^{(2,IND)}_{n\{\Lambda\}}$

The induction terms $W_{n\{\Lambda\}}^{(2,IND)}$ given in Eq.(2.28) are computed order by order in vdw.f90//induction. The loop structures in this routine are quite simple, with only book keeping of the various terms adding any complication.

A.12 Evaluation of $W_{n\{\Lambda\}}^{(2,DIS)}$

The evaluation of the dispersion terms $W_{n\{\Lambda\}}^{(2,DIS)}$ given in Eq.(2.28) provide a particular set of programming problems to address. Namely the double sum over excited states and the large index space in { Λ } gives a scaling of $N_{k_A}N_{k_B}N_{\{\Lambda\}}$ with N_i being the length of that index. To give a sense of scale, a typical calculation involving H₂ with a large basis set can produce a Fock space of $N_{K_A} > 1000$, resulting in over 5×10^8 individual elements to the nested sums. In fact larger molecule calculations have resulting in computation sizes on the order of 10^9 . With this in mind, any programming optimization can result in significant speedups.

Firstly, the precomputation of $\tilde{\zeta}_{L_1L_2L}^{\ell_0\ell'_1;\ell_2\ell'_2}$ (Eq.(2.26)) nets nearly a factor of two speedup due to the computational cost of evaluating factorials. Secondly the use of OpenMP threading reduces the computational cost significantly. The way the threading was implemented is to thread the loop over { Λ } while serializing the outer summations over k_i . Below is the overview of the n = 6 loops, the OpenMP calls are prefaced by !\$OMP, with a preprocessor ifcheck for implementation ease.

```
!do c6 first, this breaks out the loops for easier access
do na = 1,A%nstate
    do nb = 1, B\%nstate
        dd = A\% eigev(na) + B\% eigev(nb)
#ifdef iOPENMP
!$OMP PARALLEL PRIVATE(t11A,t11B) SHARED(t6)
!$OMP DO
#endif
        do ii = 1, vv6\%indsize
             t11A = tcont11(A, vv6\%iL1(ii), vv6\%ik1(ii), na)
             t11B = tcont11(B, vv6\%iL2(ii), vv6\%ik2(ii), nb)
             t6(ii) = t11A * t11B
        end do !ii
#ifdef iOPENMP
!$OMP END DO
!$OMP END PARALLEL
#endif
!compiler will vectorize this
        vv6\%vdwc6 = vv6\%vdwc6 + t6/dd
    end do !nb
end do !na
```

A.13 PROG

quick file summary Controlling routine: driver.f90 file io, reading etc : io.f90 math routines: mlib.f90 memory control, data structure definitions, printout: sms.f90 van der waals routines: vdw.f90 tensor contractor include: ctcont.h functions include: function.h io definition include: io.h parameter and thresholding include: thresh.h subroutines: driver.f90:subroutine help driver.f90:subroutine test (A,B,vv) io.f90:subroutine getcmnd(cmndnum,cmndnn,buffr,ierr) io.f90:**subroutine** openfo(recrd, fname) io.f90:**subroutine** openfn(recrd, fname) io.f90:**subroutine** readtm(A) io.f90:subroutine readvdw(vv,vv3,vv4,vv5,vv6,vv7,vv8) io.f90:**subroutine** readrho(lf) io.f90:!subroutine legacyreadtm(A) mlib.f90:subroutine Qtlookup(A) mlib.f90:**subroutine** Ttlookup(i,tm,A) mlib.f90:**subroutine** generateclebg(A) mlib.f90:**subroutine** indskel(vv) mlib.f90: !subroutine legacytlookup (A) sms.f90:subroutine initiate (A) sms.f90:subroutine createm(A) sms.f90:subroutine destroym(A) sms.f90:subroutine createvdwind(vv) sms.f90:subroutine destroyvdwind(vv) sms.f90:subroutine makelf(lf) sms.f90:subroutine createlf(lf) sms.f90:subroutine destroylf(lf) sms.f90:subroutine printskel(vv) sms.f90:subroutine printrc(lfA,lfB,vvlf) sms.f90:subroutine vdwcoefprint(A,B,vv,vv3,vv4,vv5,vv6,vv7,vv8) vdw.f90:subroutine polarizability(A,vv) vdw.f90:subroutine electrostatic (A, B, vv, vv3, vv4, vv5) vdw.f90:subroutine induction(A,B,vv,vv6,vv7,vv8) vdw. f90: **subroutine** dispersion (A, B, vv, vv6, vv8) vdw.f90:subroutine rcouple(A,B,vv,vv3,vv4,vv5,vv6,vv7,vv8,vvlf,lfA,lfB) functions: mlib.f90:recursive function ft(k) result(factorial) mlib.f90:function zeta (l1,l1p,l2,l2p,lambda1,lambda2,lambda) mlib.f90:function eta(L1, L2, L, M)mlib.f90:function tcont(A, l1, l2, L, M, istate) result(tprod)

mlib.f90:function tcont11(A,L,M, istate) result(tprod) mlib.f90:function tcont12(A,L,M, istate) result(tprod) mlib.f90:function tcont13(A,L,M,istate) result(tprod) mlib.f90:function tcont22(A,L,M, istate) result(tprod) mlib.f90:function Atcont11(A,L,M) result(tprod) mlib.f90:function Atcont12(A,L,M) result(tprod) mlib.f90:function Atcont13(A,L,M) result(tprod) mlib.f90:function Atcont22(A,L,M) result(tprod) mlib.f90:function Qtcont11(A,L,M) result(tprod) mlib.f90:function Qtcont12(A,L,M) result(tprod) mlib.f90:function Qtcont13(A,L,M) result(tprod) mlib.f90:function Qtcont22(A,L,M) result(tprod) Makefile: EXEC=smsab mSRC=sms.f90 SRC=driver.f90 io.f90 mlib.f90 vdw.f90 OBJ= (mSRC: . f90=.o) \$ (SRC: . f90=.o) CERNPATH=. CERN_MLIB=-lmathlib CERNFLG=-L\$(CERNPATH)/ \$(CERN_MLIB) -lgfortran IPATH=/opt/intel/composerxe OMP_INC=\$(IPATH)/include #opt flags FFopt=-g -O3 -funroll-loops -vec-report0 #omp flags FFomp=-openmp PPomp=-DiOPENMP #debug flags, do not use with FFopt FFdbg=-g -check PPdbg=-Didbg #verbose preproc PPverb=Diverb #legacy field couple preproc PPllf = -DiLLFLDFLAG=\$(CERNFLG) INC=-I\$ (OMP_INC) PREPROC=-fpp \$(PPomp) \$(PP11f) FC=ifort \$(INC) \$(FFopt) \$(FFomp) \$(PREPROC) #PREPROC=-fpp \$(PPdbg) \$(PPverb) \$(PPllf) #FC=ifort \$(INC) \$(FFdbg) \$(FFverb) \$(PREPROC) F77=fort \$(FCopt) CC=icc
Appendix B

Def2 additional diffuse basis functions

B.1 Lithium

L	i			
S	1	1		
	1		0.010570024365	1.0000000
\mathbf{S}		1		
	1		0.005285012182	1.0000000
Р		1		
	1		0.010244979620	1.0000000
Р		1		
	1		0.005122489810	1.0000000
D		1		
	1		0.03785000	1.0000000
D		1		
	1		0.01892500	1.0000000
\mathbf{F}		1		
	1		0.06750000	1.0000000
\mathbf{F}		1		
	1		0.03375000	1.0000000

B.2 Sodium

Ν	a			
\mathbf{S}		1		
	1		0.00775453	1.0000000
\mathbf{S}		1		
	1		0.00387726	1.0000000
Р		1		
	1		0.00775453	1.0000000
Р		1		
_	1		0.00387726	1.0000000
D	4	1	0.00505000	1 000000
Б	T	4	0.03785000	1.000000
D	1	1	0.01000500	1 000000
F	1	1	0.01892500	1.000000
г		T		

1		0.06750000	1.0000000
F	1	0.00055000	1 0000000
1		0.03375000	1.0000000

B.3 Potassium

Κ		
S 1		
1	0.00852788	1.0000000
P 1		
1	0.00765000	1.0000000
D 1		
1	0.02700000	1.0000000
F 1		
1	0.04500000	1.0000000

B.4 Rubidium

Rb				
\mathbf{S}		1		
1	1		0.00652570	1.0000000
Р		1		
1	1		0.00642350	1.0000000
D		1		
1	1		0.00476768	1.0000000
F		1		
1	1		0.03829000	1.0000000

B.5 Cesium

C	5			
\mathbf{S}		1		
	1		0.00549805	1.0000000
Р		1		
	1		0.00542271	1.0000000
D		1		
	1		0.00570469	1.0000000
\mathbf{F}		1		
	1		0.03500000	1.0000000

Appendix C

Sample van der Waals program

```
program test
      implicit real *8(a-h, o-z)
      character title *80
      dimension na(100), l1a(100), l2a(100), ma(100), w(100)
\mathbf{c}
      energy conversion factors (from Molpro manual)
\mathbf{c}
е
      data tok/3.157733d5/,
                                    tocm/219474.63067d0/
      data tohz/6.5796838999d15/,tokj/2625.500d0/
      data tokcal/627.5096d0/
      data pi/3.14159265359D+00/
\mathbf{c}
      evaluate long range interaction potential
с
с
      using Eq. 20 of vdW MS.
с
      read(5, '(a)') title
      write(6, '(a)') title
      read(5,*) nt
      do i=1,nt
        read(5,*) na(i), l1a(i), l2a(i), ma(i), w(i)
      enddo
\mathbf{c}
      write(6,100)
      fact = pi / 180.d0
      do k=1,10000
        read(5, *, end=999) r, th1, ph1, th2, ph2
        vt = 0.d0
        do i=1,nt
           cs1 = cos(fact*th1)
           cs2 = cos(fact*th2)
           cs3 = cos(ma(i)*fact*(ph1-ph2))
           tmp = w(i) * plm(l1a(i), ma(i), cs1)
     $
                      *plm(12a(i),ma(i),cs2)*cs3/r**na(i)
           if(l1a(i).ne.l2a(i)) tmp = 2.d0*tmp
           if(na(i).gt.5) tmp = -tmp
           vt = vt + tmp
\mathbf{c}
        enddo
        write(6,101) r, th1, ph1, th2, ph2, vt, vt*tocm, vt*tok
```

```
enddo
  999 continue
\mathbf{c}
  100 format('_____theta1__phi1____theta2__phi2____e(au)',
     $ '____e(cm-1)____e(K) ')
  101 format (5 f8.3, f14.8, 2 f10.4)
      end
*deck plm
      real*8 function plm(1,m,x)
      implicit real *8(a-h,o-z)
\mathbf{c}
      dumb routine to calculate first few
\mathbf{c}
\mathbf{c}
      associated legendre polynomials (from table)
с
      s = sqrt((1.d0 - x)*(1.d0 + x))
      if(1.eq.0) then
        plm = 1.d0
      else if (l.eq.1) then
         if(m.eq.0) plm = x
         if(m.eq.1) plm = -s
      else if(1.eq.2) then
         if(m.eq.0) plm = (3.d0 * x * x - 1.d0)/2.d0
         if(m.eq.1) plm = -3.d0*x*s
         if(m.eq.2) plm = 3.d0*s*s
      else if (l.eq.3) then
         if(m.eq.0) plm = (5.d0 * x * x * x - 3.d0 * x)/2.d0
         if(m.eq.1) plm = -1.5d0*(5.d0*x*x - 1.d0)*s
         if(m.eq.2) plm = 15.d0*x*s*s
         if(m.eq.3) plm = -15.d0*s*s*s
      else if (1.eq.4) then
         if(m.eq.0) plm = (35.d0 * x * x * x * x - 30.d0 * x * x + 3.d0)/8.d0
         if(m.eq.1) plm = -2.5d0*(7.d0*x*x*x - 3.d0*x)*s
         if(m.eq.2) plm = 7.5 d0 * (7.d0 * x * x - 1.d0) * s * s
         if(m.eq.3) plm = -105.d0 * x * s * s * s
         if(m.eq.4) plm = 105.d0*s*s*s*s
      else
         write(6,*) 'bad_arguments', l, m
         call exit
      endif
      return
      end
```

C.1 Sample Input

$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$												
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Na2	—	Na2	PBE	0	(see 1	Fig.	2)				
	26					-	-	,				
	5	2	2	0		664.						
	5	2	2	1		-147.6	3					
	5	2	2	2		9.223	3					
	6	0	0	0		4.073	3d3					
	6	2	0	0		5.487	$7 \mathrm{d}2$					
	6	2	2	0		2.470)d2					
	6	2	2	1		-5.489	9d1					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6	2	2	2		6.861	$1\mathrm{d}0$					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	0	0	0		5.777	$7\mathrm{d}5$					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	2	0	0		3.082	$2\mathrm{d}5$					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	2	2	0		8.025	$5\mathrm{d}4$					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	2	2	1		-1.109	9d4					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	2	2	2		4.481	l d2					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	4	0	0		1.253	3d4					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	4	2	0		7.528	3d3					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	4	2	1		-9.951	1d2					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	4	2	2		5.047	7d1					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	0	0	0		7.459	9d4					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	2	0	0		4.802	2 d4					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	2	2	0		1.928	8d4					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	2	2	1		-3.855	5d3					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	2	2	2		9.639)d2					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	4	0	0		3.197	7d4					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	4	2	0		2.545	5d4					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	4	2	1		-3.470)d3					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8	4	2	2		1.928	3d2					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	20	1	0.	0.	0	. 0.						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	30	1	0.	0.	0	. 0.						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	40	(0.	0.	0	. 0.						
60 0. 0. 0. 0.	50	(0.	0.	0	. 0.						
	60	1	0.	0.	0	. 0.						

C.2 Sample Output

Na2 - Na2	PBE0 (se	e Fig.	2)				
r	theta1	phi1	theta2	phi2	e(au)	e(cm-1)	e(K)
20.000	0.000	0.000	0.000	0.000	0.00005960	13.0812	18.820
30.000	0.000	0.000	0.000	0.000	0.00001743	3.8245	5.502
40.000	0.000	0.000	0.000	0.000	0.0000491	1.0787	1.551
50.000	0.000	0.000	0.000	0.000	0.0000174	0.3811	0.548
60.000	0.000	0.000	0.000	0.000	0.0000073	0.1598	0.229

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