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Long-range interactions between alkali Rydberg atom pairs correlated to the ns – ns , np – np and nd – nd asymptotes

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Abstract

We have calculated the long-range interaction potential curves of highly excited Rydberg atom pairs for the combinations Li–Li, Na–Na, K–K, Rb–Rb and Cs–Cs in a perturbative approach. The dispersion C -coefficients are determined for all symmetries of molecular states that correlate to the ns – ns , np – np and nd – nd asymptotes. Fitted parameters are given for the scaling of the C -coefficients as a function of the principal quantum number n for all homonuclear pairs of alkali metal atoms.

 This article has associated online supplementary data files

1. Introduction

With the development of modern laser cooling and trapping techniques the investigation of Rydberg atoms has entered a new realm. Gases of Rydberg atoms can be prepared at densities exceeding 10^{10} cm^{-3} and at temperatures in the micro-Kelvin range ('frozen Rydberg gas' [1, 2]). In this regime, long-range van-der-Waals interactions are no longer masked by thermal motion and even ultralong range Rydberg molecules may be created [3]. The interaction between Rydberg atoms leads to density-dependent line broadening of resonances [4, 6], modification of collisional processes [7] and molecular resonances due to avoided crossings [8]. A spectacular consequence of the long-range Rydberg–Rydberg interactions is the inhibition of Rydberg excitation in a confined gas of atoms [5, 6]. This effect, coined 'dipole blockade', can be exploited to realize elements for quantum computation [9] with particular emphasis on mesoscopic ensembles [10]. To make quantitative predictions

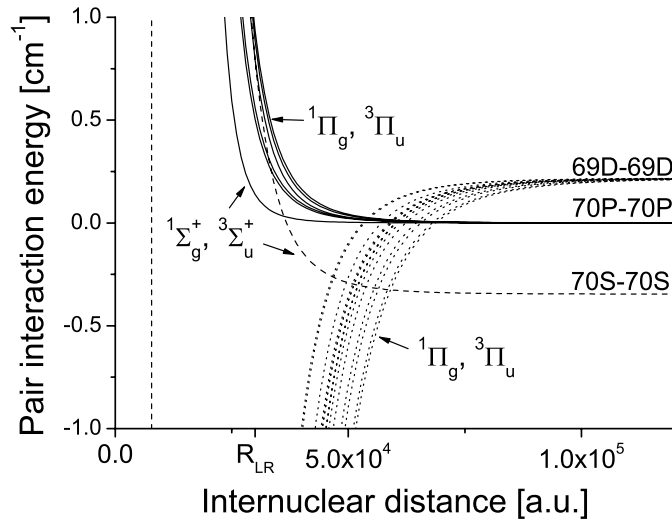


Figure 1. Potential curves for the different symmetries of 70p–70p (solid lines), 70s–70s (dashed line) and 69d–69d (dotted lines) of lithium. R_{LR} denotes the Le Roy radius.

and to interpret measured data, one needs to obtain accurate values for the long-range van-der-Waals interaction potentials. Interaction potentials for the np – np asymptotes of states with low principal quantum numbers have been obtained in a perturbative approach by Marinescu [11] based on asymptotic interaction terms described by Dalgarno *et al* [12]. This approach has been extended to high Rydberg states in [3].

In this paper we present explicit expressions for long-range interaction potentials between Rydberg atoms in s, p and d angular momentum states. We will focus on homonuclear dimers where both atoms are in the same state. Rydberg atoms are the ideal candidate as they have very large polarizabilities leading to pronounced van-der-Waals interaction between mutually induced dipoles. We evaluate the three leading C -dispersion coefficients of the asymptotic interaction potential $V(R)$ given as an expansion of the interatomic distance R , i.e. $V(R) \simeq -C_6/R^6 - C_8/R^8 - C_{10}/R^{10}$ (ns – ns asymptote), $-C_5/R^5 - C_6/R^6 - C_8/R^8$ (np – np asymptote) and $-C_5/R^5 - C_6/R^6 - C_7/R^7$ (nd – nd asymptote). Our calculations are applied to alkali atoms, since most experiments with cold Rydberg gases use these elements. As an example the potential curves for lithium around $n = 70$ are plotted in figure 1. We give the values of the C -coefficients as a function of n in terms of simple fitting parameters.

The paper is organized as follows: in section 2 we review the basic steps in the calculation of the interaction potentials following the approach of Marinescu [11]. The unperturbed wavefunctions for the ns – ns , np – np and nd – nd asymptotes are listed in section 3. Simple fitting parameters are given for the coefficients for arbitrary symmetries and different alkali metals. For some cases an additional resonance term is included. Concluding remarks are made in section 4. A detailed description of the calculation of the radial wavefunctions for alkali Rydberg atoms can be found in appendix A supplied as online supplementary data (stacks.iop.org/JPhysB/38/S295). Explicit expressions for the van-der-Waals coefficients are also supplied in appendix B as online supplementary data (stacks.iop.org/JPhysB/38/S295). We have also set up a web interface where the reader can calculate interaction potentials for cases not treated here [13].

2. Theoretical concepts

2.1. Interaction potential

The interaction energy between two atoms separated by large internuclear distances R can be expanded as an infinite sum of powers of $1/R$ [12]

$$V(\vec{r}_1, \vec{r}_2) = - \sum_{n=1}^{\infty} \frac{C_n}{R^n} = \sum_{\ell, L=1}^{\infty} \frac{V_{\ell L}(\vec{r}_1, \vec{r}_2)}{R^{\ell+L+1}} \quad (1)$$

with \vec{r}_1 and \vec{r}_2 the relative positions of each electron with respect to the atom core, and

$$V_{\ell L}(\vec{r}_1, \vec{r}_2) = \frac{(-1)^L 4\pi}{\sqrt{(2\ell+1)(2L+1)}} \sum_m \sqrt{\binom{\ell+L}{\ell+m} \binom{\ell+L}{L+m}} r_1^\ell r_2^L Y_{\ell m}(\hat{r}_1) Y_{L-m}(\hat{r}_2), \quad (2)$$

where $\binom{n}{k} = n!/(k!(n-k)!)$ is the binomial coefficient and $Y_{\ell m}(\hat{r})$ are spherical harmonics. In order for equations (1) and (2) to be valid, the electron wavefunctions of the two atoms must not overlap so that exchange and charge overlap interactions can be neglected. This is the case if R is larger than the Le Roy radius R_{LR} [14]:

$$R_{LR} = 2(\langle n_1 \ell_1 | r^2 | n_1 \ell_1 \rangle^{1/2} + \langle n_2 \ell_2 | r^2 | n_2 \ell_2 \rangle^{1/2}), \quad (3)$$

where $\langle n_1 \ell_1 | r^2 | n_1 \ell_1 \rangle$ are the matrix elements of r^2 between the radial wavefunctions belonging to the valence electron of an alkali atom. Then the energy shift due to the long-range interaction can be calculated by using perturbation theory, taking the interaction potential (1) as a perturbation to the Hamiltonian for the noninteracting asymptotic case.

2.2. Symmetries

All geometric symmetry operations of homonuclear diatomic molecules form the point group $D_{\infty h}$. The symmetry elements that we usually consider are rotations about the internuclear axis, reflections (σ_v) through a plane containing the rotation axis and the inversion i of the spatial coordinates at the centre point between both atom cores [15]. Multiple applications of these symmetry operations generate the whole point group. The group symmetry gives the classification of molecular states and some good quantum numbers. The molecular wavefunctions are naturally expressed in the molecule-fixed coordinate system. The projection of the total angular momentum $M = m_1 + m_2$ onto the molecular axis is conserved as a consequence of the rotation symmetry. If $M \neq 0$, reflections through a plane containing the molecular axis change the sign of the projection of the angular momentum on the axis. For $M \neq 0$, the reflected molecular state has the same energy as the initial one. Consequently, the (anti)symmetrization $|M^\pm\rangle = (1 \pm \sigma_v)/\sqrt{2}|M\rangle$ of the $M \neq 0$ states does not break the degeneracy between the states with the same absolute value of M . Only for Σ -states (i.e. $M = 0$) the (anti)symmetrization $|\Sigma^\pm\rangle = (1 \pm \sigma_v)/\sqrt{2}|\Sigma\rangle$ can give nondegenerate states, and thus the symmetry property under reflections can be used to distinguish different molecular potentials. It turns out that the representation of the reflection operator σ_v in the molecule-fixed coordinate system is not unique because the position of the symmetry axis of a linear molecule is determined only by two Euler angles [16]. The absence of off-axis nuclei impedes a unique definition of the way how the third Euler angle is transformed under the space-fixed inversion giving an additional phase factor in the representation of σ_v . This factor is fixed by an additional convention [16].

In case $M = m_1 = m_2 = 0$ for the $n\ell-n\ell$ asymptotes there can exist only Σ^+ states, as it follows from equation (4). The inversion operation i inverts the single electronic state

relative to the respective atom core and then translates the state to the other atom core so that the first electron is located near the second atom core and vice versa. As $i \times i = 1$ the eigenvalues p of i must be either +1 or -1. Molecular states which do not change the sign of the spatial wavefunction under this symmetry operation are labelled *gerade* states and those that change sign are labelled *ungerade* states. To fulfil the condition that the total electronic wavefunction is antisymmetric under exchange of both electrons, the spatial part of the total wavefunction must be symmetric for the antisymmetric singlet spin state, and antisymmetric for the symmetric triplet spin states.

Defining $\sigma = (-1)^S$ with the total spin S , the proper symmetrized spatial part of the electronic wavefunction of the homonuclear atom pair has the following asymptotic form:

$$\begin{aligned} |_{n_2 l_2 m_2}^{n_1 l_1 m_1}, M; \sigma; p\rangle \simeq \{ & [|n_1 l_1 m_1; \vec{R}_1\rangle |n_2 l_2 m_2; \vec{R}_2\rangle + \sigma p (-1)^{l_1+l_2} |n_2 l_2 m_2; \vec{R}_1\rangle |n_1 l_1 m_1; \vec{R}_2\rangle] \\ & + (-1)^{l_1+l_2} p [|n_1 l_1 m_1; \vec{R}_2\rangle |n_2 l_2 m_2; \vec{R}_1\rangle \\ & + \sigma p (-1)^{l_1+l_2} |n_2 l_2 m_2; \vec{R}_2\rangle |n_1 l_1 m_1; \vec{R}_1\rangle\}, \end{aligned} \quad (4)$$

where n_1 and n_2 are the principal quantum number, l_1 and l_2 the angular momentum quantum numbers, and m_1 and m_2 the separate projections of the angular momentum of each atom onto the molecular axis satisfying the constraint $M = m_1 + m_2$. In our notation, the ket $|n_i l_i m_i; R_k\rangle |n_j l_j m_j; R_{k'}\rangle$ means that the first electron is in state $n = n_i, l = l_i$ and $m = m_i$ while the second electron is in state $n = n_j, l = l_j$ and $m = m_j$. R_k and $R_{k'}$ are the positions of the two nuclei k and k' (with $k, k' = 1, 2$). It is further understood in the following way by letting the bra $\langle \vec{r}_1 | \langle \vec{r}_2 |$ act from the left:

$$\langle \vec{r}_1 | n_i l_i m_i; \vec{R}_k \rangle \langle \vec{r}_2 | n_j l_j m_j; \vec{R}_{k'} \rangle = \Phi_{n_i l_i m_i}(\vec{r}_1 - \vec{R}_k) \Phi_{n_j l_j m_j}(\vec{r}_2 - \vec{R}_{k'}), \quad (5)$$

with \vec{r}_1 and \vec{r}_2 denoting the absolute position vectors to the first and second electrons and $\Phi_{nlm}(\vec{r}) = R_{nl}(r) Y_{lm}(\hat{r})$ being the spatial wavefunction for the electron of an single atom, where $R_{nl}(r)$ represents its radial wavefunction and the spherical harmonic $Y_{lm}(\hat{r})$ its angular wavefunction. In the appendix, we give a detailed description on the calculation of the radial wavefunctions for alkali Rydberg atoms.

2.3. Expressions for C -coefficients

In order to obtain the expressions for the C -coefficients, perturbation theory is applied. The interaction potential $V(\vec{r}_1, \vec{r}_2)$ in equation (1) is taken as a perturbation to the Hamiltonian of a noninteracting atom pair, H_0 . The total Hamiltonian H has the following form:

$$H = H_0 + V(\vec{r}_1, \vec{r}_2). \quad (6)$$

As unperturbed zero order molecular wavefunctions, the asymptotic expressions (4) of the preceding sections are used. The first-order energy shift for nondegenerate states is obtained by calculating the expectation values of V defined in equation (1) with respect to the selected state

$$\Delta E^{(1)} = \langle_{n_2 l_2, m_2}^{n_1 l_1, m_1}, M; \sigma; p | V |_{n_2 l_2, m_2}^{n_1 l_1, m_1}, M; \sigma; p \rangle. \quad (7)$$

Symmetry considerations show that M , σ and p are good quantum numbers which are not mixed by Hamiltonian (6) even when looking at higher order perturbation terms. If $R > R_{LR}$ the electron wavefunctions for each atom do not overlap so that mutual terms between the first square bracket and the second square bracket of equation (4) are zero. Additionally perturbation terms evaluated for the first square bracket are the same as for the second square bracket since the only difference in the states is a permutation of the position vectors of the two nuclei. As a consequence we can further simplify the expression for the unperturbed

zero order wavefunction (4) by reducing it to the proper normalized first square bracket. This greatly simplifies the calculations and therefore equation (7) can be rewritten as

$$\frac{1}{2} \left[\langle n_1 \ell_1 m_1 | + \sigma p (-1)^{\ell_1 + \ell_2} \langle n_2 \ell_2 m_2 | \right] V \left[|n_2 \ell_2 m_2 \rangle + \sigma p (-1)^{\ell_1 + \ell_2} |n_1 \ell_1 m_1 \rangle \right], \tag{8}$$

with $M = m_1 + m_2$ and the notation

$$\left| \begin{smallmatrix} n_1 \ell_1 m_1 \\ n_2 \ell_2 m_2 \end{smallmatrix} \right\rangle := |n_1 \ell_1 m_1 \rangle |n_2 \ell_2 m_2 \rangle. \tag{9}$$

From equation (8) we can see a twofold degeneracy between singlet gerade and triplet ungerade states and between singlet ungerade and triplet gerade states as the Hamiltonian (6) is spin independent and no matrix elements depend separately on σ and p but only on the product σp . This degeneracy is removed at closer distances since the mutual contributions of the two square brackets of equation (4) are not negligible and the matrix elements of (6) start to depend on p and $p\sigma$. Under the condition $R > R_{LR}$ we can take equation (8) so that we have to sum matrix elements of the following form,

$$\begin{aligned} \langle \begin{smallmatrix} n'_1 \ell'_1 m'_1 \\ n'_2 \ell'_2 m'_2 \end{smallmatrix} | V_{\ell L} | \begin{smallmatrix} n_1 \ell_1 m_1 \\ n_2 \ell_2 m_2 \end{smallmatrix} \rangle &= \frac{(-1)^L 4\pi}{\sqrt{(2\ell+1)(2L+1)}} \sum_m \sqrt{\binom{\ell+L}{\ell+m} \binom{\ell+L}{L+m}} \\ &\times \langle n'_1 \ell'_1 | r^\ell | n_1 \ell_1 \rangle \langle n'_2 \ell'_2 | r^L | n_2 \ell_2 \rangle \langle \ell'_1 m'_1 | Y_{\ell m} | \ell_1 m_1 \rangle \langle \ell'_2 m'_2 | Y_{L-m} | \ell_2 m_2 \rangle, \end{aligned} \tag{10}$$

where $\langle n' \ell' | r^k | n \ell \rangle$ is the matrix element of r^k

$$\langle n' \ell' | r^k | n \ell \rangle = \int_0^\infty R_{n' \ell'}(r) r^k R_{n \ell}(r) r^2 dr, \tag{11}$$

and $\langle \ell' m' | Y_{LM} | \ell m \rangle$ is the matrix element of the spherical harmonics which can be expressed as [11]

$$\begin{aligned} \langle \ell' m' | Y_{LM} | \ell m \rangle &= \int Y_{\ell' m'}^*(\hat{r}) Y_{LM}(\hat{r}) Y_{\ell m}(\hat{r}) d\Omega \\ &= (-1)^{m'} \sqrt{\frac{(2\ell'+1)(2L+1)(2\ell+1)}{4\pi}} \begin{pmatrix} \ell' & L & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & L & \ell \\ -m' & M & m \end{pmatrix}, \end{aligned} \tag{12}$$

where the two terms in brackets are the Wigner 3j symbols defined in [17, 18] and can be calculated by using the Racah formula [19].

For degenerate zero-order molecular states $|M^{(i)}\rangle$, degenerate perturbation theory has to be applied. In order to find the correct eigenvectors the following matrix has to be diagonalized:

$$\begin{pmatrix} \langle M^{(1)} | V | M^{(1)} \rangle & \langle M^{(1)} | V | M^{(2)} \rangle & \dots \\ \langle M^{(2)} | V | M^{(1)} \rangle & \langle M^{(2)} | V | M^{(2)} \rangle & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}.$$

The eigenvalues are the first-order energy shifts and the eigenvectors are the zero-order basis states. We obtain molecular states of the same symmetry and asymptotic energies but with different interaction potentials.

The energy correction in the second-order perturbation has the form

$$\Delta E^{(2)} = \sum_{\phi_i} \frac{\langle \begin{smallmatrix} n_1 \ell_1 m_1 \\ n_2 \ell_2 m_2 \end{smallmatrix}, M; \sigma; p | V | \phi_i \rangle \langle \phi_i | V | \begin{smallmatrix} n_1 \ell_1 m_1 \\ n_2 \ell_2 m_2 \end{smallmatrix}, M; \sigma; p \rangle}{E_M - E_{M_i}}, \tag{13}$$

where the sum is over a complete orthogonal basis set. Like in the first-order case, we have to sum matrix elements of the following form,

Table 1. Unperturbed molecular states for different symmetries according to Wigner and Witmer [20]. States with equal $|M|$ and symmetry are asymptotically degenerate and are obtained by degenerate perturbation theory.

$ M $	Symmetry	Representation for the ns - ns asymptote
0	$^1\Sigma_g^+, ^3\Sigma_u^+$	$\begin{pmatrix} n00\rangle \\ n00\rangle \end{pmatrix}$
$ M $	Symmetry	Representation for the np - np asymptote
2	$^1\Delta_g, ^3\Delta_u$	$\begin{pmatrix} n11\rangle \\ n11\rangle \end{pmatrix}$
1	$^1\Pi_u, ^3\Pi_g$	$\frac{1}{\sqrt{2}} (n10\rangle - n11\rangle)$
1	$^1\Pi_g, ^3\Pi_u$	$\frac{1}{\sqrt{2}} (n10\rangle + n11\rangle)$
0	$^1\Sigma_u^-, ^3\Sigma_g^-$	$\frac{1}{\sqrt{2}} (n1-1\rangle - n11\rangle)$
0	$^1\Sigma_g^+, ^3\Sigma_u^+$	$\sqrt{\frac{2}{3}} n10\rangle + \frac{1}{\sqrt{6}} n1-1\rangle + \frac{1}{\sqrt{6}} n1-1\rangle$
0	$^1\Sigma_g^+, ^3\Sigma_u^+$	$-\frac{1}{\sqrt{3}} n10\rangle + \frac{1}{\sqrt{3}} n1-1\rangle + \frac{1}{\sqrt{3}} n1-1\rangle$
$ M $	Symmetry	Representation for the nd - nd asymptote
4	$^1\Gamma_g, ^3\Gamma_u$	$\begin{pmatrix} n22\rangle \\ n22\rangle \end{pmatrix}$
3	$^1\Phi_u, ^3\Phi_g$	$\frac{1}{\sqrt{2}} (n21\rangle - n22\rangle)$
3	$^1\Phi_g, ^3\Phi_u$	$\frac{1}{\sqrt{2}} (n21\rangle + n22\rangle)$
2	$^1\Delta_u, ^3\Delta_g$	$\frac{1}{\sqrt{2}} (n20\rangle - n22\rangle)$
2	$^1\Delta_g, ^3\Delta_u$	$\sqrt{\frac{8}{19}} n20\rangle + \sqrt{\frac{8}{19}} n20\rangle + \sqrt{\frac{3}{19}} n21\rangle$
2	$^1\Delta_g, ^3\Delta_u$	$-\sqrt{\frac{3}{38}} n20\rangle - \sqrt{\frac{3}{38}} n20\rangle + \frac{4}{\sqrt{19}} n21\rangle$
1	$^1\Pi_u, ^3\Pi_g$	$\sqrt{\frac{1}{4} + \frac{7}{4\sqrt{55}}} (n20\rangle - n21\rangle) + \sqrt{\frac{1}{4} - \frac{7}{4\sqrt{55}}} (n2-1\rangle - n22\rangle)$
1	$^1\Pi_u, ^3\Pi_g$	$\sqrt{\frac{1}{4} - \frac{7}{4\sqrt{55}}} (- n20\rangle + n20\rangle) + \sqrt{\frac{1}{4} + \frac{7}{4\sqrt{55}}} (n2-1\rangle - n22\rangle)$
1	$^1\Pi_g, ^3\Pi_u$	$\sqrt{\frac{1}{4} - \frac{5}{4\sqrt{79}}} (- n20\rangle - n20\rangle) + \sqrt{\frac{1}{4} + \frac{5}{4\sqrt{79}}} (n2-1\rangle + n2-1\rangle)$
1	$^1\Pi_g, ^3\Pi_u$	$\sqrt{\frac{1}{4} + \frac{5}{4\sqrt{79}}} (n20\rangle + n20\rangle) + \sqrt{\frac{1}{4} - \frac{5}{4\sqrt{79}}} (n2-1\rangle + n2-1\rangle)$
0	$^1\Sigma_u^-, ^3\Sigma_g^-$	$\frac{1}{\sqrt{5+\sqrt{5}}} (n2-1\rangle - n2-1\rangle) + \frac{1}{\sqrt{5-\sqrt{5}}} (n2-2\rangle - n2-2\rangle)$
0	$^1\Sigma_u^-, ^3\Sigma_g^-$	$\frac{1}{\sqrt{5-\sqrt{5}}} (- n2-1\rangle + n2-1\rangle) + \frac{1}{\sqrt{5+\sqrt{5}}} (n2-2\rangle - n2-2\rangle)$
0	$^1\Sigma_g^+, ^3\Sigma_u^+$	$0.4121 (n2-1\rangle + n2-1\rangle) + 0.5204 (n2-2\rangle + n2-2\rangle) + 0.3445 n20\rangle$
0	$^1\Sigma_g^+, ^3\Sigma_u^+$	$-0.1316 (n2-1\rangle + n2-1\rangle) - 0.2064 (n2-2\rangle + n2-2\rangle) + 0.9382 n20\rangle$
0	$^1\Sigma_g^+, ^3\Sigma_u^+$	$-0.5593 (n2-1\rangle + n2-1\rangle) + 0.4320 (n2-2\rangle + n2-2\rangle) + 0.0331 n20\rangle$

$$\begin{aligned}
& \sum_{\substack{n_1 l_1 m_1 \\ n_2 l_2 m_2}} \frac{\langle n_1' l_1' m_1' | V | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | V | n_2 l_2 m_2 \rangle}{(E_{n_1 l_1} + E_{n_2 l_2}) - (E_{n_1 l_1} + E_{n_2 l_2})} \\
&= \sum_{l, L, l', L'=1}^{\infty} \frac{1}{R^{l+L+l'+L'+2}} \sum_{\substack{n_1 l_1 m_1 \\ n_2 l_2 m_2}} \frac{\langle n_1' l_1' m_1' | V_{l'L'} | n_1 l_1 m_1 \rangle \langle n_2 l_2 m_2 | V_{l'L'} | n_2 l_2 m_2 \rangle}{(E_{n_1 l_1} + E_{n_2 l_2}) - (E_{n_1 l_1} + E_{n_2 l_2})} \quad (14)
\end{aligned}$$

and the sum is over all possible intermediate states. To simplify the notation, we define the following matrix:

$$\langle n_2' l_2' m_2' | W_{l'L'} | n_1 l_1 m_1 \rangle = \sum_{\substack{n_i l_i m_i \\ n_j l_j m_j}} \frac{\langle n_1' l_1' m_1' | V_{l'L'} | n_i l_i m_i \rangle \langle n_j l_j m_j | V_{l'L'} | n_2 l_2 m_2 \rangle}{(E_{n_1 l_1} + E_{n_2 l_2}) - (E_{n_i l_i} + E_{n_j l_j})}. \quad (15)$$

Table 2. Dispersion coefficients of high Rydberg states for the ns – ns , np – np and nd – nd asymptotes of Li–Li. The coefficients are scaled by their major dependence on n and the residual dependence is fitted using three fitting parameters as indicated in the table.

ns – ns	$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_8 = n^{15}(c_0 + c_1n + c_2n^2)$			$C_{10} = n^{22}(c_0 + c_1n + c_2n^2)$		
Symmetry	c_0 ($\times 10^1$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-4}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^{-2}$)	c_2 ($\times 10^{-4}$)	c_0 ($\times 10^{-3}$)	c_1 ($\times 10^{-5}$)	c_2 ($\times 10^{-7}$)
$^1\Sigma_g^+, ^3\Sigma_u^+$	–1.594	–1.045	5.690	5.039	–2.935	1.207	–2.501	4.376	–2.189 ^a
np – np	$C_5 = n^8(c_0 + c_1n + c_2n^2)$			$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_8 = n^{15}(c_0 + c_1n + c_2n^2)$		
Symmetry	c_0 ($\times 10^0$)	c_1 ($\times 10^{-2}$)	c_2 ($\times 10^{-4}$)	c_0 ($\times 10^0$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^0$)	c_2 ($\times 10^{-2}$)
$^1\Delta_g, ^3\Delta_u$	–1.190	–0.539	0.293	–2.806	–1.220	0.623	–0.669	–0.721	0.365
$^1\Pi_u, ^3\Pi_g$		Vanishes		–2.147	–1.264	0.648	–5.381	–3.450	1.750
$^1\Pi_g, ^3\Pi_u$	4.778	2.128	–1.167	–6.177	–2.193	1.123	3.187	–0.979	0.476 ^b
$^1\Sigma_u^-, ^3\Sigma_g^-$		Vanishes		–4.763	–1.692	0.862	–2.789	–1.518	0.768
$^1\Sigma_g^+, ^3\Sigma_u^+$	–7.168	–3.192	1.750	9.326	–1.852	0.932	7.914	–3.963	1.953 ^c
$^1\Sigma_g^+, ^3\Sigma_u^+$		Vanishes		–2.105	–1.161	0.599	–0.166	–0.990	0.506
nd – nd	$C_5 = n^8(c_0 + c_1n + c_2n^2)$			$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_7 = n^{12}(c_0 + c_1n + c_2n^2)$		
Symmetry	c_0 ($\times 10^0$)	c_1 ($\times 10^{-4}$)	c_2 ($\times 10^{-5}$)	c_0 ($\times 10^2$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^{-2}$)	c_2 ($\times 10^{-4}$)
$^1\Gamma_g, ^3\Gamma_u$	–3.011	–11.670	0.710	1.307	0.716	–0.448	0.787	0.382	–0.232
$^1\Phi_u, ^3\Phi_g$	–1.506	–5.836	0.355	1.356	0.722	–0.453	–0.197	–0.095	0.058
$^1\Phi_g, ^3\Phi_u$	4.517	17.510	–1.064	2.973	1.707	–1.062	–3.345	–1.622	0.985
$^1\Delta_u, ^3\Delta_g$	3.513	13.620	–0.828	2.719	1.545	–0.962	1.181	0.572	–0.348
$^1\Delta_g, ^3\Delta_u$	3.262	12.650	–0.769	4.229	0.391	–0.298	4.226	2.048	–1.244
$^1\Delta_g, ^3\Delta_u$	–1.506	–5.829	0.353	2.043	–0.022	–0.021	0.104	0.050	–0.030
$^1\Pi_u, ^3\Pi_g$	–2.112	–8.186	0.498	2.835	–0.685	0.361	–1.675	–0.812	0.493
$^1\Pi_u, ^3\Pi_g$	1.610	6.241	–0.379	2.785	0.858	–0.554	–1.277	–0.619	0.376
$^1\Pi_g, ^3\Pi_u$	2.481	9.618	–0.585	2.464	1.384	–0.863	0.508	0.246	–0.150
$^1\Pi_g, ^3\Pi_u$	–1.979	–7.673	0.466	6.314	–2.499	1.390	–0.311	–0.151	0.092
$^1\Sigma_u^-, ^3\Sigma_g^-$	–4.872	–18.890	1.148	4.772	–1.749	0.968	2.848	1.381	–0.838
$^1\Sigma_u^-, ^3\Sigma_g^-$	1.861	7.214	–0.439	2.476	1.139	–0.717	1.088	0.527	–0.320
$^1\Sigma_g^+, ^3\Sigma_u^+$	–5.728	–22.200	1.350	5.951	–3.028	1.711	0.887	0.430	–0.261
$^1\Sigma_g^+, ^3\Sigma_u^+$	–2.650	–10.270	0.624	3.500	–1.182	0.647	–3.751	–1.818	1.104
$^1\Sigma_g^+, ^3\Sigma_u^+$	0.850	3.293	–0.200	2.403	0.643	–0.421	–1.071	–0.519	0.315

^a The following resonance term has to be added to the polynomial:

$$C_{10} = n^{22}(c_0 + c_1n + c_2n^2 + 1.493 \times 10^{-2}/(n - 22.91)).$$

^b The following resonance term has to be added to the polynomial:

$$C_8 = n^{15}(c_0 + c_1n + c_2n^2 + 3.377 \times 10^1/(n - 38.50) + 8.523/(n - 44.49)).$$

^c The following resonance term has to be added to the polynomial:

$$C_8 = n^{15}(c_0 + c_1n + c_2n^2 + 1.012 \times 10^2/(n - 38.50) + 2.561 \times 10^1/(n - 44.49)).$$

The calculational effort is simplified by the following symmetry properties:

$$\begin{aligned}
\langle n'_1\ell'_1m'_1 | V_{\ell L} | n_1\ell_1m_1 \rangle &= (-1)^{\ell+L} \langle n'_2\ell'_2m'_2 | V_{\ell L} | n_2\ell_2m_2 \rangle \\
&= \langle n'_1\ell'_1-m'_1 | V_{\ell L} | n_1\ell_1-m_1 \rangle \\
&= \langle n_1\ell_1m_1 | V_{\ell L} | n'_2\ell'_2m'_2 \rangle.
\end{aligned} \tag{16}$$

Also, $\langle n'_1\ell'_1m'_1 | V_{\ell L} | n_1\ell_1m_1 \rangle = 0$ if at least one of the following conditions is true:

Table 3. Dispersion coefficients of high Rydberg states for the ns – ns , np – np and nd – nd asymptotes of Na–Na. The coefficients are scaled by their major dependence on n and the residual dependence is fitted using three fitting parameters as indicated in the table.

ns – ns	$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_8 = n^{15}(c_0 + c_1n + c_2n^2)$			$C_{10} = n^{22}(c_0 + c_1n + c_2n^2)$		
	c_0 ($\times 10^0$)	c_1 ($\times 10^0$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^0$)	c_1 ($\times 10^0$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^{-2}$)	c_1 ($\times 10^{-4}$)	c_2 ($\times 10^{-6}$)
$^1\Sigma_g^+, ^3\Sigma_u^+$	8.586	–1.464	5.820	–5.315	–1.357	6.757	–1.435	3.343	–2.022
np – np	$C_5 = n^8(c_0 + c_1n + c_2n^2)$			$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_8 = n^{15}(c_0 + c_1n + c_2n^2)$		
	c_0 ($\times 10^0$)	c_1 ($\times 10^{-2}$)	c_2 ($\times 10^{-4}$)	c_0 ($\times 10^0$)	c_1 ($\times 10^{-2}$)	c_2 ($\times 10^{-4}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^0$)	c_2 ($\times 10^{-3}$)
$^1\Delta_g, ^3\Delta_u$	–0.974	–0.895	0.483	–0.014	–1.999	1.053	–1.325	–0.520	2.726
$^1\Pi_u, ^3\Pi_g$	Vanishes			1.267	–1.177	0.608	–3.427	–1.510	7.896
$^1\Pi_g, ^3\Pi_u$	3.895	3.582	–1.931	–1.672	–4.771	2.527	–1.556	–0.624	3.261
$^1\Sigma_u^-, ^3\Sigma_g^-$	Vanishes			–1.483	–3.796	2.013	–0.987	–0.463	2.416
$^1\Sigma_g^+, ^3\Sigma_u^+$	–5.819	–5.484	2.995	138.900	4.101	–2.313 ^a	–1.238	–1.414	7.436
$^1\Sigma_g^+, ^3\Sigma_u^+$	Vanishes			1.090	–1.175	0.617	–2.118	–0.953	5.049
nd – nd	$C_5 = n^8(c_0 + c_1n + c_2n^2)$			$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_7 = n^{12}(c_0 + c_1n + c_2n^2)$		
	c_0 ($\times 10^0$)	c_1 ($\times 10^{-4}$)	c_2 ($\times 10^{-5}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^{-2}$)	c_2 ($\times 10^{-4}$)
$^1\Gamma_g, ^3\Gamma_u$	–2.993	–14.930	0.888	2.571	0.522	–0.503	0.780	0.509	–0.301
$^1\Phi_u, ^3\Phi_g$	–1.496	–7.464	0.444	3.164	0.540	–0.522	–0.195	–0.127	0.075
$^1\Phi_g, ^3\Phi_u$	4.489	22.390	–1.331	4.005	1.193	–1.145	–3.314	–2.162	1.280
$^1\Delta_u, ^3\Delta_g$	3.492	17.410	–1.035	4.062	1.090	–1.047	1.170	0.763	–0.452
$^1\Delta_g, ^3\Delta_u$	3.242	16.170	–0.961	5.527	1.645	–1.573	4.187	2.731	–1.617
$^1\Delta_g, ^3\Delta_u$	–1.496	–7.464	0.444	4.369	0.786	–0.756	0.103	0.067	–0.040
$^1\Pi_u, ^3\Pi_g$	–2.099	–10.470	0.622	5.349	1.075	–1.031	–1.659	–1.082	0.641
$^1\Pi_u, ^3\Pi_g$	1.600	7.981	–0.475	4.148	1.098	–1.053	–1.265	–0.825	0.489
$^1\Pi_g, ^3\Pi_u$	2.466	12.300	–0.731	3.908	0.987	–0.949	0.503	0.328	–0.194
$^1\Pi_g, ^3\Pi_u$	–1.967	–9.812	0.583	8.193	2.376	–2.265	–0.308	–0.201	0.119
$^1\Sigma_u^-, ^3\Sigma_g^-$	–4.842	–24.150	1.436	6.051	1.800	–1.716	2.822	1.841	–1.090
$^1\Sigma_u^-, ^3\Sigma_g^-$	1.850	9.225	–0.549	4.076	0.985	–0.946	1.078	0.703	–0.416
$^1\Sigma_g^+, ^3\Sigma_u^+$	–5.693	–28.390	1.688	7.510	2.223	–2.117	0.878	0.573	–0.339
$^1\Sigma_g^+, ^3\Sigma_u^+$	–2.633	–13.130	0.781	6.032	1.320	–1.263	–3.716	–2.424	1.435
$^1\Sigma_g^+, ^3\Sigma_u^+$	0.844	4.211	–0.250	4.065	0.944	–0.906	–1.061	–0.692	0.410

^a The following resonance term has to be added to the polynomial:

$$C_6 = n^{11}(c_0 + c_1n + c_2n^2 + 6.736 \times 10^3/(n - 55.49)).$$

$$\begin{aligned}
 \ell'_1 + \ell_1 + \ell &= (\text{odd}), & \ell'_2 + \ell_2 + L &= (\text{odd}) \\
 m'_1 + m'_2 &\neq m_1 + m_2, \\
 \ell < |\ell'_1 - \ell_1|, & \ell > \ell'_1 + \ell_1, & L < |\ell'_2 - \ell_2|, & L > \ell'_2 + \ell_2.
 \end{aligned}
 \tag{17}$$

The symmetry properties of $\langle n'_1 \ell'_1 m'_1 | W_{\ell L}^{\ell' L'} | n_1 \ell_1 m_1 \rangle$ are

$$\begin{aligned}
 \langle n'_1 \ell'_1 m'_1 | W_{\ell L}^{\ell' L'} | n_1 \ell_1 m_1 \rangle &= (-1)^{\ell + \ell' + L + L'} \langle n'_2 \ell'_2 m'_2 | W_{L \ell}^{L' \ell'} | n_2 \ell_2 m_2 \rangle \\
 &= \langle n'_1 \ell'_1 - m'_1 | W_{\ell L}^{\ell' L'} | n_1 \ell_1 - m_1 \rangle \\
 &= \langle n_1 \ell_1 m_1 | W_{\ell L}^{\ell' L'} | n'_2 \ell'_2 m'_2 \rangle.
 \end{aligned}
 \tag{18}$$

Table 4. Dispersion coefficients of high Rydberg states for the ns – ns , np – np and nd – nd asymptotes of K–K. The coefficients are scaled by their major dependence on n and the residual dependence is fitted using three fitting parameters as indicated in the table.

ns – ns	$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_8 = n^{15}(c_0 + c_1n + c_2n^2)$			$C_{10} = n^{22}(c_0 + c_1n + c_2n^2)$		
Symmetry	c_0 ($\times 10^0$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^0$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^{-3}$)	c_1 ($\times 10^{-4}$)	c_2 ($\times 10^{-6}$)
$^1\Sigma_g^+, ^3\Sigma_u^+$	1.827	–4.352	2.054	2.955	3.950	–2.016	–9.594	2.115	–1.234
np – np	$C_5 = n^8(c_0 + c_1n + c_2n^2)$			$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_8 = n^{15}(c_0 + c_1n + c_2n^2)$		
Symmetry	c_0 ($\times 10^0$)	c_1 ($\times 10^{-2}$)	c_2 ($\times 10^{-4}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^0$)	c_2 ($\times 10^{-2}$)
$^1\Delta_g, ^3\Delta_u$	–0.571	–1.508	0.794	–0.012	–3.592	1.680	0.610	1.704	–0.811
$^1\Pi_u, ^3\Pi_g$		Vanishes		0.015	–7.296	3.388	1.950	–0.358	0.139
$^1\Pi_g, ^3\Pi_u$	2.284	6.031	–3.177	–0.056	–1.910	0.923	0.716	3.082	–1.456
$^1\Sigma_u^-, ^3\Sigma_g^-$		Vanishes		–0.047	–0.900	0.447	1.165	0.662	–0.342
$^1\Sigma_g^+, ^3\Sigma_u^+$	–3.426	–9.046	4.766	2.698	–4.285	2.154	6.016	–5.126	2.227
$^1\Sigma_g^+, ^3\Sigma_u^+$		Vanishes		0.012	–6.510	3.024	1.509	0.763	–0.396
nd – nd	$C_5 = n^8(c_0 + c_1n + c_2n^2)$			$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_7 = n^{12}(c_0 + c_1n + c_2n^2)$		
Symmetry	c_0 ($\times 10^0$)	c_1 ($\times 10^{-3}$)	c_2 ($\times 10^{-5}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-4}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-4}$)
$^1\Gamma_g, ^3\Gamma_u$	–2.645	–7.505	4.154	–0.381	–0.423	2.301	0.646	0.279	–1.537
$^1\Phi_u, ^3\Phi_g$	–1.322	–3.753	2.077	–0.628	–0.643	3.497	–0.162	–0.070	0.384
$^1\Phi_g, ^3\Phi_u$	3.967	11.260	–6.231	–0.004	–0.207	1.115	–2.747	–1.187	6.531
$^1\Delta_u, ^3\Delta_g$	3.086	8.756	–4.846	–0.190	–0.353	1.911	0.970	0.419	–2.305
$^1\Delta_g, ^3\Delta_u$	2.865	8.131	–4.500	0.412	–0.396	2.206	3.471	1.500	–8.249
$^1\Delta_g, ^3\Delta_u$	–1.322	–3.753	2.077	–0.574	–0.901	4.933	0.085	0.037	–0.202
$^1\Pi_u, ^3\Pi_g$	–1.855	–5.264	2.913	–0.349	–1.014	5.584	–1.376	–0.594	3.270
$^1\Pi_u, ^3\Pi_g$	1.414	4.013	–2.221	–0.069	–0.417	2.285	–1.049	–0.453	2.493
$^1\Pi_g, ^3\Pi_u$	2.179	6.184	–3.423	–0.277	–0.413	2.241	0.417	0.180	–0.992
$^1\Pi_g, ^3\Pi_u$	–1.739	–4.934	2.731	1.152	–0.827	4.674	–0.256	–0.110	0.608
$^1\Sigma_u^-, ^3\Sigma_g^-$	–4.280	–12.140	6.721	0.914	–0.556	3.154	2.339	1.011	–5.560
$^1\Sigma_u^-, ^3\Sigma_g^-$	1.635	4.638	–2.567	–0.309	–0.497	2.707	0.893	0.386	–2.124
$^1\Sigma_g^+, ^3\Sigma_u^+$	–5.031	–14.280	7.902	1.297	–0.750	4.267	0.728	0.315	–1.731
$^1\Sigma_g^+, ^3\Sigma_u^+$	–2.327	–6.604	3.655	–0.104	–1.048	5.793	–3.081	–1.331	7.323
$^1\Sigma_g^+, ^3\Sigma_u^+$	0.746	2.117	–1.172	–0.275	–0.566	3.096	–0.880	–0.380	2.091

Again, $\langle n_1' \ell_1' m_1' | W_{\ell L}^{\ell' L'} | n_2 \ell_2 m_2 \rangle = 0$ if at least one of the following conditions is true:

$$\begin{aligned}
 \ell_1 + \ell_1' + \ell + \ell' &= (\text{odd}), & \ell_2 + \ell_2' + L + L' &= (\text{odd}) \\
 m_1' + m_2' &\neq m_1 + m_2 \\
 |\ell_1' - \ell'| > \ell_1 + \ell, & & |\ell_1 - \ell| > \ell_1' + \ell' \\
 |\ell_2' - L'| > \ell_2 + L, & & |\ell_2 - L| > \ell_2' + L'.
 \end{aligned} \tag{19}$$

3. Evaluation of potentials

In what follows, the interaction potentials for Rydberg states correlated to the ns – ns , np – np and nd – nd asymptotes of alkali atoms are obtained by taking equation (1) as a perturbation. In our approach, the fine structure is neglected, and we choose the centre of gravity as the

Table 5. Dispersion coefficients of high Rydberg states for the ns – ns , np – np and nd – nd asymptotes of Rb–Rb. The coefficients are scaled by their major dependence on n and the residual dependence is fitted using three fitting parameters as indicated in the table. All nd – nd C_6 coefficients show resonances. They have to be differently calculated as indicated in the table with $n_0 = 35.14$.

ns – ns	$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_8 = n^{15}(c_0 + c_1n + c_2n^2)$			$C_{10} = n^{22}(c_0 + c_1n + c_2n^2)$		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
Symmetry	($\times 10^1$)	($\times 10^{-1}$)	($\times 10^{-3}$)	($\times 10^0$)	($\times 10^{-1}$)	($\times 10^{-3}$)	($\times 10^{-4}$)	($\times 10^{-6}$)	($\times 10^{-9}$)
$^1\Sigma_g^+, ^3\Sigma_u^+$	1.197	–8.486	3.385	–7.303	8.068	–3.792	–5.546	5.242	–3.154
np – np	$C_5 = n^8(c_0 + c_1n + c_2n^2)$			$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_8 = n^{15}(c_0 + c_1n + c_2n^2)$		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
Symmetry	($\times 10^0$)	($\times 10^{-2}$)	($\times 10^{-2}$)	($\times 10^{-1}$)	($\times 10^{-1}$)	($\times 10^{-4}$)	($\times 10^1$)	($\times 10^0$)	($\times 10^{-2}$)
$^1\Delta_g, ^3\Delta_u$	–0.231	–1.976	0.010	3.620	–0.579	2.778	1.199	–0.624	0.250
$^1\Pi_u, ^3\Pi_g$	Vanishes			6.070	–1.273	6.157	1.173	0.010	–0.069
$^1\Pi_g, ^3\Pi_u$	0.922	7.903	–0.041	3.575	–0.183	0.816	2.973	–2.281	0.990
$^1\Sigma_u^-, ^3\Sigma_g^-$	Vanishes			2.373	–0.034	0.107	2.176	–1.711	0.747
$^1\Sigma_g^+, ^3\Sigma_u^+$	–1.383	–11.850	0.061	43.010	3.575	–1.714 ^a	5.359	–3.984	1.729
$^1\Sigma_g^+, ^3\Sigma_u^+$	Vanishes			5.461	–1.133	5.476	0.712	0.244	–0.162
nd – nd	$C_5 = n^8(c_0 + c_1n + c_2n^2)$			$C_6 = n^{11}(c_0 + c_1n + \frac{c_{-1}}{n-n_0})$			$C_7 = n^{11}(c_0 + c_1n + c_2n^2)$		
	c_0	c_1	c_2	c_0	c_1	c_{-1}	c_0	c_1	c_2
Symmetry	($\times 10^0$)	($\times 10^{-2}$)	($\times 10^{-4}$)	($\times 10^1$)	($\times 10^{-2}$)	($\times 10^0$)	($\times 10^1$)	($\times 10^{-1}$)	($\times 10^{-1}$)
$^1\Gamma_g, ^3\Gamma_u$	–1.445	–2.731	1.477	2.603	1.454	66.310	0.235	0.920	–0.487
$^1\Phi_u, ^3\Phi_g$	–0.722	–1.366	0.738	4.124	2.475	105.000	–0.059	–0.230	0.122
$^1\Phi_g, ^3\Phi_u$	2.167	4.097	–2.215	0.643	–0.273	16.570	–0.997	–3.911	2.069
$^1\Delta_u, ^3\Delta_g$	1.686	3.186	–1.723	1.730	0.525	44.200	0.352	1.380	–0.730
$^1\Delta_g, ^3\Delta_u$	1.565	2.959	–1.600	0.571	–0.584	14.650	1.260	4.940	–2.614
$^1\Delta_g, ^3\Delta_u$	–0.722	–1.366	0.738	5.157	3.032	131.200	0.031	0.121	–0.064
$^1\Pi_u, ^3\Pi_g$	–1.013	–1.915	1.036	5.157	2.864	131.200	–0.499	–1.958	1.036
$^1\Pi_u, ^3\Pi_g$	0.773	1.460	–0.789	1.789	0.563	45.640	–0.381	–1.493	0.790
$^1\Pi_g, ^3\Pi_u$	1.191	2.250	–1.217	2.217	0.916	56.570	0.151	0.594	–0.314
$^1\Pi_g, ^3\Pi_u$	–0.950	–1.795	0.971	0.907	–0.779	22.990	–0.093	–0.364	0.193
$^1\Sigma_u^-, ^3\Sigma_g^-$	–2.338	–4.419	2.389	0.274	–0.870	6.928	0.849	3.330	–1.762
$^1\Sigma_u^-, ^3\Sigma_g^-$	0.893	1.688	–0.913	2.676	1.229	68.210	0.324	1.272	–0.673
$^1\Sigma_g^+, ^3\Sigma_u^+$	–2.748	–5.195	2.809	0.298	–1.100	7.455	0.264	1.037	–0.548
$^1\Sigma_g^+, ^3\Sigma_u^+$	–1.271	–2.403	1.299	4.755	2.449	120.900	–1.118	–4.386	2.320
$^1\Sigma_g^+, ^3\Sigma_u^+$	0.408	0.771	–0.417	2.942	1.436	74.940	–0.319	–1.252	0.663

^a The following resonance term has to be added to the polynomial:

$$C_6 = n^{11}(c_0 + c_1n + c_2n^2 + 6.931 \times 10^2/(n - 29.5)).$$

energy of $n\ell$ states. The np – np case has already been extensively discussed and analysed in [3, 11]. The nd – nd symmetries have also a C_7 coefficient arising from the first order-correction to the energy. The determination of the C_5 and C_7 coefficients, as well as the higher order corrections, is facing additional difficulties from the asymptotic degenerate states for which the C_7 does not vanish. In these cases, even the zeroth-order wavefunctions depend on the internuclear distance R . In order to get C_5 and C_7 for those states, one needs to diagonalize the matrix of the first-order correction to the energy and then expand its eigenvalues in powers of $1/R$. The matrices are of the following type,

$$R^{-5}(M_0 + R^{-2}M_1), \quad (20)$$

where equation (20) represents the right-hand side of equation (1) in the set of the degenerate

Table 6. Dispersion coefficients of high Rydberg states for the ns – ns , np – np and nd – nd asymptotes of Cs–Cs. The coefficients are scaled by their major dependence on n and the residual dependence is fitted using three fitting parameters as indicated in the table.

ns – ns	$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_8 = n^{15}(c_0 + c_1n + c_2n^2)$			$C_{10} = n^{22}(c_0 + c_1n + c_2n^2)$		
	c_0 ($\times 10^1$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^0$)	c_2 ($\times 10^{-2}$)	c_0 ($\times 10^{-3}$)	c_1 ($\times 10^{-5}$)	c_2 ($\times 10^{-7}$)
$^1\Sigma_g^+, ^3\Sigma_u^+$	1.064	–6.249	2.330	–3.019	3.777	–1.581	3.190	–5.920	3.022
np – np	$C_5 = n^8(c_0 + c_1n + c_2n^2)$			$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_8 = n^{15}(c_0 + c_1n + c_2n^2)$		
	c_0 ($\times 10^0$)	c_1 ($\times 10^{-2}$)	c_2 ($\times 10^{-4}$)	c_0 ($\times 10^{-1}$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^1$)	c_1 ($\times 10^0$)	c_2 ($\times 10^{-2}$)
$^1\Delta_g, ^3\Delta_u$	–0.070	–1.973	0.940	–2.886	0.571	–0.268	–0.774	1.044	–0.445
$^1\Pi_u, ^3\Pi_g$		Vanishes		–0.738	0.346	–0.168	–4.270	4.239	–1.793
$^1\Pi_g, ^3\Pi_u$	0.279	7.893	–3.759	–8.121	1.349	–0.625	0.402	–0.093	0.031
$^1\Sigma_u^-, ^3\Sigma_g^-$		Vanishes		–6.577	1.072	–0.496	0.031	0.088	–0.042
$^1\Sigma_g^+, ^3\Sigma_u^+$	–0.418	–11.840	5.638	133.400	6.850	–3.074 ^a	–1.569	1.747	–0.765
$^1\Sigma_g^+, ^3\Sigma_u^+$		Vanishes		–0.839	0.337	–0.163	–2.671	3.045	–1.289
nd – nd	$C_5 = n^8(c_0 + c_1n + c_2n^2)$			$C_6 = n^{11}(c_0 + c_1n + c_2n^2)$			$C_7 = n^{12}(c_0 + c_1n + c_2n^2)$		
	c_0 ($\times 10^0$)	c_1 ($\times 10^{-2}$)	c_2 ($\times 10^{-4}$)	c_0 ($\times 10^0$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-3}$)	c_0 ($\times 10^0$)	c_1 ($\times 10^{-1}$)	c_2 ($\times 10^{-3}$)
$^1\Gamma_g, ^3\Gamma_u$	–0.710	–3.483	1.725	0.712	–0.257	0.108	0.271	1.062	–0.504
$^1\Phi_u, ^3\Phi_g$	–0.355	–1.742	0.863	1.003	–0.151	0.053	–0.068	–0.266	0.126
$^1\Phi_g, ^3\Phi_u$	1.065	5.225	–2.588	0.641	–1.013	0.460	–1.151	–4.515	2.143
$^1\Delta_u, ^3\Delta_g$	0.828	4.064	–2.013	0.798	–0.834	0.374	0.406	1.593	–0.756
$^1\Delta_g, ^3\Delta_u$	0.769	3.774	–1.869	0.569	–1.834	0.845	1.454	5.703	–2.707
$^1\Delta_g, ^3\Delta_u$	–0.355	–1.742	0.863	1.161	–0.515	0.221	0.036	0.140	–0.066
$^1\Pi_u, ^3\Pi_g$	–0.498	–2.443	1.210	1.147	–0.999	0.448	–0.576	–2.260	1.073
$^1\Pi_u, ^3\Pi_g$	0.380	1.862	–0.922	0.721	–0.982	0.445	–0.439	–1.723	0.818
$^1\Pi_g, ^3\Pi_u$	0.585	2.870	–1.422	0.843	–0.704	0.313	0.175	0.686	–0.325
$^1\Pi_g, ^3\Pi_u$	–0.467	–2.290	1.134	0.439	–3.284	1.527	–0.107	–0.420	0.199
$^1\Sigma_u^-, ^3\Sigma_g^-$	–1.149	–5.636	2.792	0.274	–2.491	1.159	0.980	3.844	–1.825
$^1\Sigma_u^-, ^3\Sigma_g^-$	0.439	2.153	–1.066	0.896	–0.715	0.318	0.374	1.468	–0.697
$^1\Sigma_g^+, ^3\Sigma_u^+$	–1.350	–6.626	3.282	0.217	–3.262	1.521	0.305	1.197	–0.568
$^1\Sigma_g^+, ^3\Sigma_u^+$	–0.625	–3.065	1.518	1.068	–1.428	0.650	–1.290	–5.063	2.403
$^1\Sigma_g^+, ^3\Sigma_u^+$	0.200	0.983	–0.487	0.872	–0.747	0.334	–0.368	–1.446	0.686

asymptotic states. The C_5 and C_7 in these cases are

$$\begin{aligned} C_5 &= \langle n_i | M_0 | n_i \rangle, \\ C_7 &= \langle n_i | M_1 | n_i \rangle, \end{aligned} \quad (21)$$

where $|n_i\rangle$ are the eigenstates of M_0 . Note that the R^{-5} and R^{-7} interaction terms with the C_5 and C_7 given by (21) might be significantly less accurate than the eigenvalues of (20) themselves at shorter distances when R reaches the Le Roy radius R_{LR} .

Following the classification of molecular states by Wigner and Witmer [20], the molecular states are denoted by capital Greek letters ($\Sigma, \Pi, \Delta, \Phi, \dots$ for $M = 0, 1, 2, 3, \dots$). 1M and 3M represent singlet and triplet states respectively and M_g and M_u represent gerade and ungerade states respectively. The values for the C -coefficients are extracted by collecting terms with equal power of R . The explicit expressions of the perturbation terms are quite lengthy and are supplied as online supplementary data (stacks.iop.org/JPhysB/38/S295). Here we give a list of the unperturbed molecular states in table 1 for the ns – ns , np – np and nd – nd

asymptotes. The first column denotes the projection M of the total angular momentum on the internuclear axis. In the second column we give the molecular symmetry, and in the next column, the state itself.

In tables 2–6, we give the C_6 , C_8 and C_{10} coefficients for the ns – ns asymptotes, the C_5 , C_6 and C_8 coefficients for the np – np asymptotes and the C_5 , C_6 and C_7 coefficients for the nd – nd asymptotes of high Rydberg states of all alkali atoms. The C_5 , C_6 , C_7 , C_8 and C_{10} coefficients are scaled by their major dependence on n which is n^8 , n^{11} , n^{12} , n^{15} and n^{22} , respectively. The residual dependence on n is fitted for $30 \leq n \leq 95$ to a polynomial of the form $a + bn + cn^2 + \dots$, and the fitting parameters are presented in tables 2–6. A specific example is given in figure 1 where the calculated interaction potentials for Li–Li pairs near the $n \sim 70$ manifold are shown.

In a few cases, for some symmetries and some n , the two-atom levels are very close to each other and the second-order correction (13) gives large values. For these cases perturbation theory fails. We have added a resonance term of the form $c_{-1}/(n - n_0)$ to the polynomial in order to simplify the presentation of the data away from the resonance by the fitted polynomial. To check the validity of the potentials at a certain interatomic distance R we have calculated the Le Roy radius R_{LR} for different effective quantum numbers and different alkali atoms. For all alkali atoms, the Le Roy radius R_{LR} is approximately $R_{LR} \sim 5n^2$.

4. Conclusion

In this paper, we have calculated the long-range potential curves between Rydberg atoms correlated to ns – ns , np – np and nd – nd asymptotes, for all alkali atoms. We have given expressions for the dispersion coefficients as well as fitting parameters for the dependence of the C -coefficients on the principal quantum number. We have tested the numerical accuracy of our radial wavefunctions with respect to their truncation at small distance by comparing them with wavefunctions obtained using model potentials where the core is taken into account (see appendix A supplied as online supplementary data (stacks.iop.org/JPhysB/38/S295)). We also tested the convergence of our results as a function of the number of intermediate states (n') included, and found that convergence to the five significant digit was attained by taking $n - 20 \leq n' \leq n + 20$ (n being the principal quantum number of the state under consideration).

The results presented here do not take into account corrections due to spin–orbit coupling (fine structure). These effects appear as differences in the quantum defect of $p_{1/2}$ and $p_{3/2}$, or $d_{3/2}$ and $d_{5/2}$, and may play a role especially for Rb and Cs. For these two species, we used the centre-of-gravity for the energy level entering the second-order perturbation expressions, and the quantum defect of $j = \ell - 1/2$ for the radial matrix elements of the various multipole moments (which are not very sensitive to the j component used). As an estimate of the error introduced by neglecting the spin–orbit interaction we performed calculations replacing the centre-of-gravity energy by the energy of one of the fine structure components. At $n = 60$ for rubidium some C_6 dispersion coefficients obtained by second-order perturbation theory deviate by a factor of 3–5. It should also be noted that the resonance is shifted from $n = 35$ to $n = 38$. We intend to tackle this issue in a future work.

We have found that in most cases, the dispersion coefficients follow simple scaling behaviours, the variation from those being well fitted by simple polynomials. However, in a few instances, we found *divergent* coefficients near some accidental degeneracies of energy levels. This is especially noticeable for the C_6 coefficient of Rb near $n = 35$. Even though in those cases perturbation theory fails we have added a resonance term to simplify our fitting procedure for coefficients far from those resonances where our calculation is valid. In future work, we intend to take into account other coupling schemes, such as Hund's case (c) instead

of (a), and include other interactions, such as exchange energies for separations smaller than the Le Roy radius, or retardation effects at very large separations.

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