PHYSICAL REVIEW A VOLUME 31, NUMBER 5 MAY 1985

van der Waals interaction in excited alkali-metal dimers

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(Received 7 September 1984)

We have studied the long-range interaction potentials of the heteronuclear alkali-metal-atom dimers in the case when one of the atoms is in the first excited state ($n_A P$) and the other is in the ground state ($n_B S$). The presentation of the general expressions for the interaction energies in the Hund's case (c) is followed by the calculation of the corresponding C_6 constants for all heteronuclear alkali-metal-atom pairs. In the case of heavier perturbers (Rb and Cs) the C_6 constants are found to be significantly influenced by the perturber's fine structure. The van der Waals interaction in the K-Rb system is exceptionally strong resulting in C_6 constants considerably larger than in all other alkali-metal-atom heteronuclear systems. The intermediate-coupling region (ICR) is defined as the region of internuclear separation R where the interaction energy is of the order of the atomic spin-orbit splitting, while the exchange energy is still negligible. Analysis of the general form of the energy matrices in the ICR shows that the homonuclear alkali-metal-atom dimers can be treated as a special case. In the large-R limit, the ICR results reduce to those obtained in Hund's case (c). As an example, we have calculated the ICR interaction potentials of the K-Rb system, taking into account only the leading dipole-dipole interaction. Finally we have discussed the construction of the absorption coefficient in the wings of the resonance lines, both in the impact and in the quasistatic approximation.

I. INTRODUCTION

The interactions and the line-broadening effects in the alkali-metal-atom vapors have been of interest for a long time. The asymmetries and satellites in the inner wings of the self-broadened first resonance lines,[1] the blue asymmetry of the potassium resonance lines broadened by rubidium[2] and by cesium,[3] or the impact broadening of the sodium resonance lines due to collisions with rubidium and with cesium[4] are just a few illustrative examples.

In the case of the first resonance lines the potential curves in question are those arising from the interaction of two alkali-metal atoms, one being in the ground state and the other in one of the first excited states. For homonuclear alkali-metal-atom pairs the resonance interaction (the first order of the perturbation theory) is usually sufficient to explain the experimental data and only in the case of Cs*-Cs interaction was there an indication of the second-order effects.[1,5] On the other hand, the relatively small difference in the excitation energies of dissimilar alkali-metal atoms yields to the strong long-range interaction of the van der Waals type (the second order of perturbation theory).

The relevant energy levels corresponding to the case of separated atoms are generally well isolated in the energy-level diagram and that fact suggests that the system can be described by the following effective Hamiltonian:

$$H_{\text{eff}} = H_0 + V_{\text{so}} + V + V_{\text{pol}} + V_{\text{ex}} , \tag{1}$$

which should be diagonalized in the chosen finite basis set of the zeroth-order wave functions.

In Eq. (1) H_0 is a sum of the Hamiltonians of the isolated atoms (with spin-orbit interaction neglected), V_{so} is a sum of the atomic spin-orbit interactions, V is a pure electrostatic interaction which gives the first-order contribution to the interaction energy, V_{pol} gives the second-order polarization contributions corresponding to the one-electron excitations (induction) and two-electron excitations (dispersion), and V_{ex} describes the exchange interaction which can be treated separately in the long-range region and thereupon simply added to give the total interaction energy.[6] In the limit of large internuclear separations the exchange energy and, in some cases, the induction energy fall off exponentially.

Neglecting the retardation effects, the whole region of the internuclear separations can be divided as follows.

(a) The region where Hund's case (c) is strictly valid, i.e., the spin-orbit interaction is the dominant one.

(b) The intermediate-coupling region where the interaction energy is of the order of the atomic spin-orbit splitting.

Up to this point the exchange interaction can be neglected and the electrostatic interaction potential can be used in the form of the multipole expansion in the powers of R^{-1}.

(c) The region where the exchange interaction becomes important and a nonexpanded form of the electrostatic interaction V is required.[7] The matrix elements of the exchange interaction can be calculated on the basis of the work of Umanskij and Voronin.[8] The matrix elements of V and V_{pol} are of the form $\sum_n (C_n R^{-n}) f_n(R)$, where $f_n(R)$ is a damping function (due to the overlap effects) with asymptotic behavior $f_n(R) \rightarrow 1$ as $R \rightarrow \infty$ and $f_n(R) \rightarrow 0$ as $R \rightarrow 0$.[7]

(d) The region of still shorter internuclear separations, where Eq. (1) is not applicable at all.

Although the effective Hamiltonian, Eq. (1), has been designed bearing in mind its application in the case of the interaction of two ground-state atoms as well as in the case of the interaction of two atoms, one being in the ground state and the other in the first excited state, a very similar approach is possible for the interaction of two excited atoms.

In the present paper we shall study the interaction potentials in the long-range region where the exchange interaction can be completely neglected, i.e., in regions (a) and (b) as defined above. Kamke *et al.*[4] have calculated van der Waals energies of Na $3P_J$ states assuming that they do not depend on the fine structure of the perturber. Although it is an excellent approximation for the case of light-alkali-metal-atom perturbers, we shall show that the interaction potentials depend strongly on the fine structure of heavier perturbers (Rb and Cs). The C_6 constants for the K-Rb pair, calculated assuming the Hund's case (c), have been published previously by Beuc *et al.*[9]

II. MATRIX ELEMENTS IN THE COUPLED REPRESENTATION

In the one-electron approximation the alkali-metal-atom wave functions are of the form $|\,nljm\,\rangle$ (coupled representation), where n, l, j, and m are the quantum numbers of the valence electron. The zeroth-order wave functions for quasimolecule $A+B$ are simply the products of the atomic wave functions $|\,n_Al_Aj_Am_A;n_Bl_Bj_Bm_B\,\rangle$, and correspond to the particular projection $M=m_A+m_B$ of the total electronic angular momentum of the system along the internuclear axis.

The H_0+V_{so} part of the H_{eff}, Eq. (1), is diagonal in the coupled representation, with the matrix elements equal to the zeroth-order energies $E(n_A,l_A,j_A)+E(n_B,l_B,j_B)$.

At large separations, where the overlap of the atomic charge distributions A and B can be neglected, the classical electrostatic interaction is usually represented by multipole expansion. If coordinate systems at A and B are oriented so that their $\mathbf{Z}$ axes coincide with the internuclear axis, the electrostatic interaction potential V can be written in the very useful form[10]

$$V=\sum_{i,j}\sum_{a,b,\alpha}\frac{4\pi e^2(-1)^b(a+b)!r_i^a r_j^b Y_a^{-\alpha}(\hat{r}_i)Y_b^{\alpha}(\hat{r}_j)}{R^{a+b+1}[(2a+1)(2b+1)(a-\alpha)!(a+\alpha)!(b-\alpha)!(b+\alpha)!]^{1/2}}\,. \tag{2}$$

$\mathbf{r}_i$ and $\mathbf{r}_j$ are the radius vectors of the ith electron in atom A and jth electron in atom B, respectively, R is the internuclear separation, and $Y_a^{-\alpha}(\hat{r}_i)$ and $Y_b^{\alpha}(\hat{r}_j)$ are spherical harmonics. For the case of two neutral atoms, a and b are both positive integers and $\alpha=0,\pm1,\ldots,\pm\min(a,b)$.

The first-order matrix element of V, Eq. (2), between two arbitrary states of the system could be evaluated in a straightforward way by using the theory of angular momentum.[10] Integrating the angular parts exactly, one finally obtains

$$\begin{aligned}
&\langle n'_Al'_Aj'_Am'_A;n'_Bl'_Bj'_Bm'_B\,|\,V\,|\,n''_Al''_Aj''_Am''_A;n''_Bl''_Bj''_Bm''_B\rangle\\
&\quad=\delta_{M'M''}(-1)^{1-M}[(2j'_A+1)(2l'_A+1)(2j'_B+1)(2l'_B+1)(2j''_A+1)(2l''_A+1)(2j''_B+1)(2l''_B+1)]^{1/2}\\
&\quad\quad\times\sum_{a,b,\alpha}\frac{e^2(-1)^b(a+b)!}{R^{a+b+1}[(a-\alpha)!(a+\alpha)!(b-\alpha)!(b+\alpha)!]^{1/2}}\langle n'_Al'_A\,|\,r_A^a\,|\,n''_Al''_A\rangle\langle n'_Bl'_B\,|\,r_B^b\,|\,n''_Bl''_B\rangle\\
&\quad\quad\quad\times\begin{pmatrix}l'_A & a & l''_A\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l'_B & b & l''_B\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}j''_A & a & j'_A\\ m''_A & -\alpha & m'_A\end{pmatrix}\begin{pmatrix}j''_B & b & j'_B\\ m''_B & \alpha & -m'_B\end{pmatrix}\begin{Bmatrix}j''_A & a & j'_A\\ l'_A & \frac{1}{2} & l''_A\end{Bmatrix}\begin{Bmatrix}j''_B & b & j'_B\\ l'_B & \frac{1}{2} & l''_B\end{Bmatrix},
\end{aligned}\tag{3}$$

where $\langle n'_Al'_A\,|\,r_A^a\,|\,n''_Al''_A\rangle$ and $\langle n'_Bl'_B\,|\,r_B^b\,|\,n''_Bl''_B\rangle$ are the atomic radial matrix elements.

The δ condition in Eq. (3) reflects the quantization of the total electronic angular momentum along the internuclear axis and allows the factorization of the secular determinant. As a consequence of the properties of 3-j symbols, the double infinite sum in Eq. (3) usually reduces to only a few terms. Namely, $l'_A+a+l''_A$ and $l'_B+b+l''_B$ should be even, triads (l'_A,a,l''_A) and (l'_B,b,l''_B) should satisfy the "triangular inequalities,"[11] and $\alpha=m''_A-m'_A=m'_B-m''_B$ if $|\,m''_A-m'_A\,|,|\,m'_B-m''_B\,|\ \le\min(a,b)$, otherwise the matrix element vanishes. For example, (see the last column of Table I), in the case $l'_B=l''_B=0$ the second 3-j symbol in Eq. (3) equals zero for any $b=1,2,\ldots$ and the first-order matrix element vanishes for any pair of the states of the system with atom B being in a S state. In another interesting case $l'_A=1$, $l'_B=0$ and $l''_A=0$, $l''_B=1$, only the term with $a=b=1$ is different from zero, i.e., in the first order the nearly resonant states of the system $A+B$ are coupled exclusively by the dipole-dipole interaction C_3R^{-3}. Furthermore, the triads (j''_A,a,j'_A) and (j''_B,b,j'_B) should also satisfy the triangular inequalities and this can further reduce the number of terms in the right-hand side of Eq. (3). So, if both atoms are, e.g., in P states, the matrix elements connecting the states $(P_{1/2})_AP_{j'_B}$ and $(P_{1/2})_AP_{j''_B}$ or $P_{j'_A}(P_{1/2})_B$ and $P_{j''_A}(P_{1/2})_B$ vanish, while all other first-order matrix elements are proportional to R^{-5} (quadrupole-quadrupole interaction).

The matrix element of V_{pol} (the second-order matrix element of V) between two states $|\,i\,\rangle$ and $|\,j\,\rangle$, belonging to the finite basis set appertaining to the H_{eff}, has a form

$$\langle i \mid V_{\text{pol}} \mid j \rangle = \sum_k \frac{\langle i \mid V \mid k \rangle \langle k \mid V \mid j \rangle}{E_k - E_i} ,$$

where the sum is taken over all states $\mid k \rangle$ not included in the basis. The $\langle i \mid V \mid k \rangle \langle k \mid V \mid j \rangle$ is explicitly given by

$$\begin{aligned}\langle n'_A l'_A j'_A m'_A ; n'_B l'_B j'_B m'_B \mid V \mid n_A l_A j_A m_A ; n_B l_B j_B m_B \rangle \langle n_A l_A j_A m_A ; n_B l_B j_B m_B \mid V \mid n''_A l''_A j''_A m''_A ; n''_B l''_B j''_B m''_B \rangle \\ = \delta_{M'M} \delta_{MM''} \sum_{\substack{a,b,\\ c,d}} \frac{e^4 (a+b)!(c+d)!}{R^{a+b+c+d+2}} \mathscr{A}_{abcd}(M'; l'_A j'_A m'_A ; l'_B j'_B ; l_A j_A m_A ; l_B j_B ; l''_A j''_A m''_A ; l''_B j''_B) \\ \times \langle n'_A l'_A \mid r_A^a \mid n_A l_A \rangle \langle n_A l_A \mid r_A^c \mid n''_A l''_A \rangle \langle n'_B l'_B \mid r_B^b \mid n_B l_B \rangle \langle n_B l_B \mid r_B^d \mid n''_B l''_B \rangle , \qquad (4)\end{aligned}$$

with

$$\begin{aligned}&\mathscr{A}_{abcd}(M'; l'_A j'_A m'_A ; l'_B j'_B ; l_A j_A m_A ; l_B j_B ; l''_A j''_A m''_A ; l''_B j''_B) \\ &\quad = (2j_A+1)(2l_A+1)(2j_B+1)(2l_B+1) \\ &\quad\quad \times [(2j'_A+1)(2l'_A+1)(2j'_B+1)(2l'_B+1)(2j''_A+1)(2l''_A+1)(2j''_B+1)(2l''_B+1)]^{1/2} \\ &\quad\quad \times \begin{bmatrix} l'_A & a & l_A \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_A & c & l''_A \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l'_B & b & l_B \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l'_B & d & l''_B \\ 0 & 0 & 0 \end{bmatrix} \\ &\quad\quad \times \frac{\begin{bmatrix} j_A & a & j'_A \\ m_A & -\alpha & -m'_A \end{bmatrix} \begin{bmatrix} j''_A & c & j_A \\ m''_A & -\beta & -m_A \end{bmatrix} \begin{bmatrix} j_B & b & j'_B \\ m_B & \alpha & -m'_B \end{bmatrix} \begin{bmatrix} j''_B & d & j_B \\ m''_B & \beta & -m_B \end{bmatrix}}{[(a-\alpha)!(a+\alpha)!(b-\alpha)!(b+\alpha)!(c-\beta)!(c+\beta)!(d-\beta)!(d+\beta)!]^{1/2}} \\ &\quad\quad \times \begin{Bmatrix} j_A & a & j'_A \\ l'_A & \frac{1}{2} & l_A \end{Bmatrix} \begin{Bmatrix} j''_A & c & j_A \\ l_A & \frac{1}{2} & l''_A \end{Bmatrix} \begin{Bmatrix} j_B & b & j'_B \\ l'_B & \frac{1}{2} & l_B \end{Bmatrix} \begin{Bmatrix} j''_B & d & j_B \\ l_B & \frac{1}{2} & l''_B \end{Bmatrix} , \qquad (5)\end{aligned}$$

where

$$\alpha = m_A - m'_A = m'_B - m_B ,$$

if

$$\mid m_A - m'_A \mid , \mid m'_B - m_B \mid \leq \min(a,b)$$

and

$$\beta = m''_A - m_A = m_B - m''_B ,$$

if

$$\mid m''_A - m_A \mid , \mid m_B - m''_B \mid \leq \min(c,d) ,$$

otherwise, some of the 3-*j* symbols in Eq. (5) vanish.

The δ condition in Eq. (4) is actually the same as in Eq. (3) and the fourfold infinite sum will reduce to a finite number of terms depending on the angular part of the intermediate state $\mid n_A l_A j_A m_A ; n_B l_B j_B m_B \rangle$. The second order matrix elements include the sum over an infinite number of intermediate state, i.e., all possible product states except those included in the basis. The useful expressions for the practical calculations could be obtained if one truncates the fourfold sum in Eq. (4) in a way that retains only the terms with R^{-n}, where $n = a + b + c + d + 2$ is smaller than some n_0. Hence, the infinite sum over the intermediate-state quantum numbers l_A and l_B will reduce to a finite number of terms, containing the information about the first few terms of the multipole expansion of the electrostatic interaction *V*, Eq. (2). For example, for $l'_A = l''_A = 1$, $l'_B = l''_B = 0$ (*PS*-*PS* interaction) it follows that $a = c = l_A + 1$, $b = d = l_B$, and for $l'_A = l''_B = 1$, $l''_A = l'_B = 0$ (*PS*-*SP* interaction) it follows that $a = l_A + 1$, $b = l_B$, $c = l_A$, and $d = l_B + 1$. In both cases the condition $a,b,c,d \geq 1$ should be satisfied. It is easy to see that in the former case the leading term in the R^{-1} expansion of the second-order matrix element is proportional to R^{-6}, while in the latter case the leading term is proportional to R^{-8}. The induction contribution ($n'_A = n_A = n''_A$, $l'_A = l_A = l''_A = 1$, $l'_B = l''_B = 0$) has the leading term proportional to R^{-8}. The intermediate states ($l_A l_B$), contributing to the second-order terms proportional to R^{-6} and R^{-8} are given in Table I.

TABLE I. The intermediate states $(l_A l_B)$ contributing to the second-order terms proportional to R^{-6} and R^{-8}. The allowed R^{-n} terms of the corresponding first-order matrix elements are given in the last column.

$l'_A l'_B l''_A l''_B$	R^{-6}	R^{-8}	First order
SSSS	*PP*	*DP,PD*	
PSPS	*SP,DP*	*PP,DP,FP,SD,DD*	
PSSP		*PP,DP,PD,DD*	R^{-3}
DSDS	*PP,FP*	*SP,PP,DP, FP,GP,PD,FD*	
PPPP	*SS,DS,SD,DD*	*PS,DS,FS,SP,DP, SD,PD,DD,FD,SF,DF*	R^{-5}
DPDP	*PS,FS,PD,FD*	*SS,PS,DS,FS,GS, PP,FP,SD,PD,DD, FD,GD,PF,FF*	R^{-5},R^{-7}
DPPD		*SS,PS,DS,FS,SP,PP, DP,FP,SD,PD,DD,FD, SF,PF,DF,FF*	R^{-3},R^{-5},R^{-7}
DDDD	*PP,FP,PF,FF*	*PS,FS,SP,PP,DP,FP, GP,PD,FD,SF,PF,DF, FF,GF,PG,FG*	R^{-5},R^{-7},R^{-9}

III. THE INTERACTION POTENTIALS FOR HUND'S CASE (c)

For the case of homonuclear alkali-metal-atom pairs the effective Hamiltonian, Eq. (1), could be taken in the simplified form $H_{\text{eff}}=H_0+V_{\text{so}}+V$ and its diagonalization is then equivalent to the first-order perturbation calculations.[1]

Let us concentrate on the case of a heteronuclear alkali-metal quasimolecule $A+B$, where one of the atoms (e.g., atom A) is in one of the first excited states $n'_A P_{j'_A}$ and the other is in the ground state $n'_B S_{1/2}$. The basis set contains now only the wave functions $|\,n'_A P j'_A m'_A ; n'_B S \tfrac{1}{2} m'_B\rangle$ with $j'_A=\tfrac{3}{2}$ *or* $j'_A=\tfrac{1}{2}$, and the diagonalization of the effective Hamiltonian, Eq. (1), is equivalent to the usual second-order perturbation calculations for the degenerate levels, because the first-order matrix elements vanish and the operator H_0+V_{so} is diagonal in the given basis, giving the zeroth-order energies $E(n'_A P_{j'_A})+E(n'_B S_{1/2})$.

According to the δ condition in Eq. (4) the secular determinants for $j'_A=\tfrac{3}{2}$ and $\tfrac{1}{2}$, respectively, factorize into subdeterminants which are distinguished by different M values. The subdeterminants with $M=\Omega$ and $-\Omega$ are equivalent in the sense that both result in the same interaction potentials, which is of course the consequence of the axial symmetry of the diatomics. The subdeterminants with $\Omega=0$ can be further factorized into two subdeterminants corresponding to $\Omega=0^+$ and 0^- states, where the superscript + or − means the point group character for the reflection in the plane containing the molecular axis.

By the choice $E(\Omega)=0$ for $R=\infty$, the interaction potentials $E(\Omega)$ are given by the following equations:

$$E(2)=\langle 1\,|\,V_{\text{pol}}\,|\,1\rangle\ , \tag{6a}$$

$$[E(1)]_{\pm}=\tfrac{1}{2}(\langle 2\,|\,V_{\text{pol}}\,|\,2\rangle+\langle 3\,|\,V_{\text{pol}}\,|\,3\rangle) \pm\tfrac{1}{2}[(\langle 2\,|\,V_{\text{pol}}\,|\,2\rangle-\langle 3\,|\,V_{\text{pol}}\,|\,3\rangle)^2 +4\,|\,\langle 2\,|\,V_{\text{pol}}\,|\,3\rangle\,|^2]^{1/2}\ , \tag{6b}$$

$$E(0^{\pm})=\langle 4\,|\,V_{\text{pol}}\,|\,4\rangle\mp\langle 4\,|\,V_{\text{pol}}\,|\,5\rangle \tag{6c}$$

for the case $A(n'_A P_{3/2})+B(n'_B S_{1/2})$, and

$$E(1)=\langle 6\,|\,V_{\text{pol}}\,|\,6\rangle\ , \tag{6d}$$

$$E(0^{\pm})=\langle 7\,|\,V_{\text{pol}}\,|\,7\rangle\pm\langle 7\,|\,V_{\text{pol}}\,|\,8\rangle \tag{6e}$$

for the case $A(n'_A P_{1/2})+B(n'_B S_{1/2})$. The wave functions $|\,i\,\rangle$ used in Eqs. (6) have the following explicit form:

$$|\,1\rangle=|\,n'_A P\,\tfrac{3}{2}\,\tfrac{3}{2};n'_B S\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle\ ,$$

$$|\,2\rangle=|\,n'_A P\,\tfrac{3}{2}\,\tfrac{1}{2};n'_B S\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle\ ,$$

$$|\,3\rangle=|\,n'_A P\,\tfrac{3}{2}\,\tfrac{3}{2};n'_B S\,\tfrac{1}{2}\,-\tfrac{1}{2}\rangle\ ,$$

$$|\,4\rangle=|\,n'_A P\,\tfrac{3}{2}\,-\tfrac{1}{2};n'_B S\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle\ ,$$

$$|\,5\rangle=|\,n'_A P\,\tfrac{3}{2}\,\tfrac{1}{2};n'_B S\,\tfrac{1}{2}\,-\tfrac{1}{2}\rangle\ ,$$

$$|\,6\rangle=|\,n'_A P\,\tfrac{1}{2}\,\tfrac{1}{2};n'_B S\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle\ ,$$

$$|\,7\rangle=|\,n'_A P\,\tfrac{1}{2}\,-\tfrac{1}{2};n'_B S\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle\ ,$$

$$|\,8\rangle=|\,n'_A P\,\tfrac{1}{2}\,\tfrac{1}{2};n'_B S\,\tfrac{1}{2}\,-\tfrac{1}{2}\rangle\ .$$

From Eq. (4) it follows that the leading term of the matrix element of V_{pol}, corresponding to the dipole-dipole interaction only, can be written in the form

$$\langle n'_A P j'_A m'_A; n'_B S \tfrac{1}{2} m'_B \,|\, V_{\text{pol}} \,|\, n'_A P j'_A m''_A; n'_B S \tfrac{1}{2} m''_B \rangle = \delta_{M'M''} \frac{4}{R^6} \sum_{l_A, j_A, j_B} \sigma(j'_A; M'; m'_A m''_A; l_A j_A j_B) \mathscr{R}(j'_A; l_A j_A j_B) \,, \tag{7}$$

where

$$\mathscr{R}(j'_A; l_A j_A j_B) = e^4 \sum_{\substack{n_A(l_A), \\ n_B(P)}} \frac{|\langle n_A l_A \,|\, r_A \,|\, n'_A P \rangle|^2 \, |\langle n_B P \,|\, r_B \,|\, n'_B S \rangle|^2}{E(n'_A P_{j'_A}) + E(n'_B S_{1/2}) - E(n_A l_A j_A) - E(n_B P_{j_B})} \,, \tag{8}$$

and the angular factor $\sigma(j'_A; M'; m_A{}' m''_A; l_A j_A j_B)$ can be obtained by summing Eq. (5), taken for $a = b = c = d = 1$, $l'_A = l''_A = 1$ and $j'_B = j''_B = \frac{1}{2}$, over m_A. The selection rules for 3-j symbols allow l_B to be 1 and l_A to be 0 or 2. Consequently $j_B = \frac{1}{2}, \frac{3}{2}$ while $j_A = \frac{1}{2}$ if $l_A = 0$ or $j_A = \frac{3}{2}, \frac{5}{2}$ if $l_A = 2$. Furthermore, for $l_A = 2$ and $j'_A = \frac{1}{2}$ the selection rules restrict j_A to be $\frac{3}{2}$ only. The preceding considerations point out that for $j'_A = \frac{3}{2}$ the nonzero matrix elements given by Eq. (7) actually consist of six parts, each of them corresponding to the sum over one of the possible types of the intermediate states: $(n_A S_{1/2} n_B P_{3/2})$, $(n_A S_{1/2} n_B P_{1/2})$, $(n_A D_{5/2} n_B P_{3/2})$, $(n_A D_{5/2} n_B P_{1/2})$, $(n_A D_{3/2} n_B P_{3/2})$, and $(n_A D_{3/2} n_B P_{1/2})$. For $j'_A = \frac{1}{2}$ the two sums containing the states $n_A D_{5/2}$ vanish as the consequence of the properties of 3-j symbols.

The right-hand side of Eq. (8) can be considerably simplified if one neglects the fine structure of all excited levels everywhere except in the first two sums containing $(n'_A S_{1/2} n'_B P_{j_B})$ nearly resonant intermediate states, in which the fine structure of the first excited doublet of atom B should appear explicitly. In the simplified form Eq. (8) reads

$$\mathscr{R}(j'_A; S \tfrac{1}{2} j_B) = \frac{C^2}{[E(n'_A P_{j'_A}) - E(n'_A S_{1/2})] - [E(n'_B P_{j_B}) - E(n'_B S_{1/2})]} + S_A \tag{9}$$

for the $l_A = 0$ case, where

$$C = e^2 \langle n'_A P \,|\, r_A \,|\, n'_A S \rangle \langle n'_B S \,|\, r_B \,|\, n'_B P \rangle \,, \tag{10}$$

$$S_A = e^4 \sum_{\substack{n_A(S), \\ n_B(P)}} \frac{|\langle n_A S \,|\, r_A \,|\, n'_A P \rangle|^2 \, |\langle n_B P \,|\, r_B \,|\, n'_B S \rangle|^2}{E(n'_A P) + E(n'_B S) - E(n_A S) - E(n_B P)} \,, \tag{11}$$

and

$$\mathscr{R}(j'_A; D j_A j_B) = e^4 \sum_{\substack{n_A(D), \\ n_B(P)}} \frac{|\langle n_A D \,|\, r_A \,|\, n'_A P \rangle|^2 \, |\langle n_B P \,|\, r_B \,|\, n'_B S \rangle|^2}{E(n'_A P) + E(n'_B S) - E(n_A D) - E(n_B P)} \equiv D_A \tag{12}$$

for $l_A = 2$ case.

The first term on the right-hand side of Eq. (9), corresponding to the nearly resonant interaction of the two atoms, has a very small energy denominator and obviously dominates the sum. It is clear that in the case of heavier-alkali-metal-atom perturbers the fine-structure influence on the energy denominator is by no means negligible.

Considering only the dipole-dipole interaction, all interaction potentials, Eq. (6) are of the form $E(\Omega) = C_6(\Omega)/R^6$. From Eqs. (6), (7), (9), and (12) follows that C_6 constants are given by

$$C_6(2) = W_1(A) + \frac{C^2}{9\beta} \,, \tag{13a}$$

$$[C_6(1)]_{\pm} = \tfrac{1}{2}(C_{\text{I}} + C_{\text{II}}) \pm \tfrac{1}{2}[(C_{\text{I}} - C_{\text{II}})^2 + 4C_{\text{III}}^2]^{1/2} \,,$$

$$C_{\text{I}} = W_1(A) + \left[\frac{2}{\alpha} + \frac{1}{\beta} \right] \frac{C^2}{27} \,,$$

$$C_{\text{II}} = W_2(A) + \left[\frac{8}{\alpha} + \frac{19}{\beta} \right] \frac{C^2}{81} \,, \tag{13b}$$

$$C_{\text{III}} = \left[\frac{1}{\alpha} - \frac{1}{\beta} \right] \frac{4\sqrt{3}C^2}{81} \,,$$

$$C_6(0^+) = W_2(A) + \left[\frac{2}{\alpha} + \frac{25}{\beta} \right] \frac{C^2}{81} \,, \tag{13c}$$

$$C_6(0^-) = W_2(A) + \left[\frac{2}{\alpha} + \frac{1}{\beta} \right] \frac{C^2}{9} \tag{13d}$$

TABLE II. C, S, and D radial terms required for calculation of C_6 constants. All quantities are given in a.u.

A-B	C	S_A	D_A	S_B	D_B
Li-Na	17.80	−1465	−2935	−3030	−5045
Li-K	20.71	−2265	−4480	−3905	−8225
Li-Rb	20.86	−2365	−4600	−4075[a]	−8695[a]
Li-Cs	22.50	−2905	−5575	−5245	−10300
Na-K	22.16	−5090	−8370	−4125	−8665
Na-Rb	22.32	−5295	−8605	−4280[a]	−9120[a]
Na-Cs	24.09	−6560	−10 510	−5510	−10 700
K-Rb	25.97	−6805	−14 250	−6805[a]	−14 250[a]
K-Cs	28.02	−8405	−17 560	−8855	−17 610
Rb-Cs	28.22	−8750[a]	−18 330[a]	−9175	−18 190

[a] Estimated values.

TABLE III. C_6 constants for all alkali-metal-atom heteronuclear pairs. In the last column the C_6 constants for ground-state atoms are given. All values are in a.u.

			$P_{3/2}$				$P_{1/2}$		$S_{1/2}$
	0^+	0^-	1	1	2	0^+	0^-	1	$0^{\pm},1$
Li*-Na	−13 070	−13 120	−13 090	−5160	−5135	−9155	−9100	−9110	−1475
Li*-K	13 980	13 670	13 860	3360	3475	8445	8745	8670	−2270
Li*-Rb	12 200	11 270	11 870	2515	2880	6675	7595	7365	−2330
Li*-Cs	7985	6955	7625	802	1215	3635	4565	4410	−2835
Na*-Li	7825	7825	7825	1265	1265	4610	4610	4610	−1475
Na*-K	3520	3445	3495	−1085	−1055	1185	1265	1245	−2420
Na*-Rb	2946	2665	2845	−1410	−1300	581	864	793	−2485
Na*-Cs	942	483	782	−2650	−2470	−1180	−717	−832	−3015
K*-Li	−22 000	−22 000	−22 000	−9525	−9525	−15 420	−15 420	−15 420	−2270
K*-Na	−14 560	−14 590	−14 570	−7175	−7165	−10 800	−10 770	−10 780	−2420
K*-Rb	200 800	134 600	181 800	35 250	65 890	85 800	187 200	161 900	−3865
K*-Cs	31 860	24 140	29 390	2935	6260	12 560	20 890	18 800	−4720
Rb*-Li	−20 670	−20 670	−20 670	−9205	−9205	−13 900	−13 900	−13 900	−2330
Rb*-Na	14 450	−14 480	−14 460	−7255	−7250	−10 550	−10 530	−10 540	−2485
Rb*-K	−232 500	−276 200	−251 400	−93 670	−79 440	−87 700	−78 750	−80 990	−3865
Rb*-Cs	40 920	30 150	37 550	4490	9200	19 660	35 790	31 750	−4855
Cs*-Li	−18 240	−18 240	−18 240	−8825	−8825	−12 370	−12 370	−12 370	−2835
Cs*-Na	−14 930	−14 950	−14 940	−7835	−7830	−10 880	−10 860	−10 870	−3015
Cs*-K	−55 140	−56 340	−55 600	−23 460	−23 020	−30 910	−30 330	−30 470	−4720
Cs*-Rb	−66 440	−75 340	−70 120	−29 590	−26 610	−37 400	−33 830	−34 720	−4855

TABLE IV. C, S, and D radial terms in the case of homonuclear alkali-metal-atom dimers. All values are in a.u.

	Li	Na	K	Rb	Cs
C	16.63	19.04	25.78	26.16	30.45
S	−1365	−3210	−6560	−7060[a]	−11 370
D	−2725	−5380	−13 830	−14 680[a]	−22 710

[a] Estimated values.

for the case $A(n'_AP_{3/2})+B(n'_BS_{1/2})$, and

$$C_6(1)=W_3(A)+\left[\frac{4}{\gamma}+\frac{14}{\delta}\right]\frac{C^2}{81}\,, \tag{13e}$$

$$C_6(0^+)=W_3(A)+\left[\frac{16}{\gamma}+\frac{2}{\delta}\right]\frac{C^2}{81}\,, \tag{13f}$$

$$C_6(0^-)=W_3(A)+\frac{2C^2}{9\delta} \tag{13g}$$

for the case $A(n'_AP_{1/2})+B(n'_BS_{1/2})$. The quantities $W_i(A)$ are defined as

$$\begin{aligned} W_1(A)&=\tfrac{1}{9}(S_A+\tfrac{19}{5}D_A)\,,\\ W_2(A)&=\tfrac{1}{3}(S_A+\tfrac{7}{5}D_A)\,,\\ W_3(A)&=\tfrac{2}{9}(S_A+2D_A)\,, \end{aligned} \tag{14}$$

and

$$\begin{aligned} \alpha&=[E(n'_AP_{3/2})-E(n'_AS_{1/2})]\\ &\quad-[E(n'_BP_{1/2})-E(n'_BS_{1/2})]\,,\\ \beta&=[E(n'_AP_{3/2})-E(n'_AS_{1/2})]\\ &\quad-[E(n'_BP_{3/2})-E(n'_BS_{1/2})]\,,\\ \gamma&=[E(n'_AP_{1/2})-E(n'_AS_{1/2})]\\ &\quad-[E(n'_BP_{1/2})-E(n'_BS_{1/2})]\,,\\ \delta&=[E(n'_AP_{1/2})-E(n'_AS_{1/2})]\\ &\quad-[E(n'_BP_{3/2})-E(n'_BS_{1/2})]\,. \end{aligned} \tag{15}$$

The atomic radial matrix elements required for calculations of C, S_A, and D_A have been deduced from known oscillator strengths according to the formula

$$|\langle nl\,|\,r\,|\,n'l'\rangle|^2=\frac{2l+1}{l_{\max}}\,\frac{3h^2}{2m_e(E_{n'l'}-E_{nl})}f(nl,n'l')\,. \tag{16}$$

Values of C, S_A, and D_A are given in Table II. Due to the lack of the relevant data, the values of S_{Rb} and D_{Rb} are only estimates. The C_6 constants for all alkali-metal-atom heteronuclear pairs are given in Table III.

Generally, the dominant contribution to the C_6 constants of the $A(n'_AP_j)+B(n'_BS_{1/2})$ pair arises from the nearly resonant intermediate states $A(n'_AS_{1/2})+B(n'_BP_j)$. In the cases $E(n'_AP_j)<E(n'_BP_j)$, all interaction potentials are attractive (negative C_6 constants), and in the cases $E(n'_AP_j)>E(n'_BP_j)$, the interaction potentials are repulsive (positive C_6 constants), except for Na*-K, Na*-Rb, and Na*-Cs pairs, where some of the interaction potentials are attractive.

An exceptionally strong interaction exists in the K-Rb system resulting in C_6 constants considerably larger than in all other alkali-metal-atom heteronuclear systems. As previously mentioned, the fine structure of the heavier-alkali-metal-atom perturbers (Rb and Cs) strongly influences the C_6 constants.

If, in the expression for the second-order matrix elements, Eq. (4), one retains not only the leading term proportional to R^{-6}, but also the next term proportional to R^{-8}, all interaction potentials, except that given by Eq. (6b), would be of the form $E=C_6R^{-6}+C_8R^{-8}$. In some cases the two potentials with $\Omega=1$, Eq. (6b), could be written in the same form if one expands the square root on the right-hand side of the Eq. (6b) in powers of R^{-1}, or alternatively, if one fits the Eq. (6b) to the form $E=C_6R^{-6}+C_8R^{-8}$, in a limited region of the internuclear separation R. In the latter approach the C_6 and C_8 constants depend on the chosen limited region.

The relatively small values of the C_6 constants for Na*-B and Li*-B cases suggests that the higher-order (C_8R^{-8}) terms may be important, as actually was demonstrated by Vadla[12] and by Vadla *et al.*[13] for Na*-K, Na*-Rb, and Li*-Cs.

IV. THE INTERACTION POTENTIALS IN THE INTERMEDIATE-COUPLING REGION

In the intermediate-coupling region the interaction energy is of the order of the atomic spin-orbit splitting δ. Furthermore, for heavier heteronuclear alkali-metal-atom pairs even the difference Δ between "uncoupled" energies of the first excited states, i.e., the energy difference between centers of gravity of the first resonance doublets, is of the same order or just a few times greater than one of the atomic spin-orbit splittings δ_A or δ_B. For these reasons the effective Hamiltonian, Eq. (1), should generally be diagonalized in the basis which contains the products of the atomic wave functions corresponding to the following energy levels of the separated atoms: $A(n_AP_{3/2})+B(n'_BS_{1/2})$, $A(n'_AP_{1/2})+B(n'_BS_{1/2})$, $A(n'_AS_{1/2})+B(n'_BP_{3/2})$, and $A(n'_AS_{1/2})+B(n'_BP_{1/2})$. The secular determinant is then of the order 24×24 and can be factorized in two 2×2 subdeterminants for the states with $\Omega=2$, two 6×6 subdeterminants for the states with $\Omega=1$ and two 4×4 subdeterminants, one for the states with $\Omega=0^+$ and the other for the states with $\Omega=0^-$.

As shown in Sec. II, the first-order nondiagonal matrix elements of V appear, which correspond to the near-resonance excitation exchange due to the relatively strong dipole-dipole interaction.

If one neglects the exchange interaction V_{ex} and takes only the dipole-dipole interaction as a perturbation, the interaction energies come from the diagonalization of the following matrices:

(a) $\Omega=2$

$$\begin{vmatrix} E_{3/2}(A)+\dfrac{W_1(A)}{R^6} & \dfrac{C}{3R^3} \\ & E_{3/2}(B)+\dfrac{W_1(B)}{R^6} \end{vmatrix} , \tag{17a}$$

(b) $\Omega=1$

$$\begin{vmatrix} E_{3/2}(A)+\dfrac{W_1(A)}{R^6} & 0 & 0 & 0 & \dfrac{\sqrt{3}C}{9R^3} & \dfrac{\sqrt{6}C}{9R^3} \\ & E_{3/2}(A)+\dfrac{W_2(A)}{R^6} & \dfrac{W_4(A)}{R^6} & \dfrac{\sqrt{3}C}{9R^3} & -\dfrac{4C}{9R^3} & \dfrac{2\sqrt{2}C}{9R^3} \\ & & E_{1/2}(A)+\dfrac{W_3(A)}{R^6} & \dfrac{\sqrt{6}C}{9R^3} & \dfrac{2\sqrt{2}C}{9R^3} & -\dfrac{2C}{9R^3} \\ & & & E_{3/2}(B)+\dfrac{W_1(B)}{R^6} & 0 & 0 \\ & & & & E_{3/2}(B)+\dfrac{W_2(B)}{R^6} & \dfrac{W_4(B)}{R^6} \\ & & & & & E_{1/2}(B)+\dfrac{W_3(B)}{R^6} \end{vmatrix} , \tag{17b}$$

(c) $\Omega=0^+$

$$\begin{vmatrix} E_{3/2}(A)+\dfrac{W_2(A)}{R^6} & \dfrac{W_4(A)}{R^6} & \dfrac{5C}{9R^3} & -\dfrac{\sqrt{2}C}{9R^3} \\ & E_{1/2}(A)+\dfrac{W_3(A)}{R^6} & -\dfrac{\sqrt{2}C}{9R^3} & \dfrac{4C}{9R^3} \\ & & E_{3/2}(B)+\dfrac{W_2(B)}{R^6} & \dfrac{W_4(B)}{R^6} \\ & & & E_{1/2}(B)+\dfrac{W_3(B)}{R^6} \end{vmatrix} , \tag{17c}$$

(d) $\Omega=0^-$

$$\begin{vmatrix} E_{3/2}(A)+\dfrac{W_2(A)}{R^6} & \dfrac{W_4(A)}{R^6} & -\dfrac{C}{3R^3} & \dfrac{\sqrt{2}C}{3R^3} \\ & E_{1/2}(A)+\dfrac{W_3(A)}{R^6} & \dfrac{\sqrt{2}C}{3R^3} & 0 \\ & & E_{3/2}(B)+\dfrac{W_2(B)}{R^6} & \dfrac{W_4(B)}{R^6} \\ & & & E_{1/2}(B)+\dfrac{W_3(B)}{R^6} \end{vmatrix} , \tag{17d}$$

where $E_j(A)$ and $E_j(B)$ have the meaning $E(n'_A Pj'_A) + E(n'_B S_{1/2})$ and $E(n'_B Pj'_B)+E(n'_A S_{1/2})$, respectively, and the quantities $W_i(A)$ giving the polarization contribution are defined by Eq. (14) and by

$$W_4(A)=-\frac{\sqrt{2}}{9}(S_A+\tfrac{1}{5}D_A) , \tag{18}$$

with S_A and D_A given by Eqs. (11) and (12), respectively, and C is given by Eq. (10). The S_B, D_B, and $W_i(B)$ are defined in the same way with B instead of A (see Table II).

Strictly speaking, in the denominators of $W_i(A)$ and $W_i(B)$ one and the same zeroth-order energy should enter, but by introducing the $E(n'_A P)$ in $W_i(A)$ and $E(n'_B P)$ in $W_i(B)$ the error made is usually less than or at most comparable to the total uncertainty due to various levels of accuracy of the oscillator strengths used.

All energy matrices (17) have the same general form:

$$\boldsymbol{M}=\begin{bmatrix}\boldsymbol{A} & \boldsymbol{C}\\ \boldsymbol{C} & \boldsymbol{B}\end{bmatrix} \tag{19}$$

with the property that besides diagonal blocks $\boldsymbol{A}$ and $\boldsymbol{B}$, the nondiagonal block $\boldsymbol{C}$ is also a real symmetric matrix, i.e., $\boldsymbol{C}^T=\boldsymbol{C}$. Furthermore, only the nondiagonal block $\boldsymbol{C}$ contains the first-order matrix elements proportional to R^{-3}. As shown in Sec. II, the leading term of the second-order matrix elements in the diagonal blocks is proportional to R^{-6}, while in the nondiagonal block it is proportional to R^{-8}. With the help of a simple unitary transformation, the matrix $\boldsymbol{M}$ can be written in the equivalent form

$$\tilde{\boldsymbol{M}}=\boldsymbol{U}^{\dagger}\boldsymbol{M}\boldsymbol{U}=\begin{bmatrix}\dfrac{\boldsymbol{A}+\boldsymbol{B}}{2}+\boldsymbol{C} & \dfrac{\boldsymbol{A}-\boldsymbol{B}}{2}\\ \dfrac{\boldsymbol{A}-\boldsymbol{B}}{2} & \dfrac{\boldsymbol{A}+\boldsymbol{B}}{2}-\boldsymbol{C}\end{bmatrix}, \tag{20}$$

where

$$\boldsymbol{U}=\frac{1}{\sqrt{2}}\begin{bmatrix}\boldsymbol{I} & \boldsymbol{I}\\ \boldsymbol{I} & -\boldsymbol{I}\end{bmatrix}, \tag{21}$$

and $\boldsymbol{I}$ is the identity matrix.

Equation (20) clearly demonstrates that in the case of the homonuclear quasimolecule ($A=B$) the further factorization of the relevant secular determinants is possible due to "gerade-ungerade" symmetry of the system. Taken without second-order terms, Eq. (20) gives the first-order results of Movre and Pichler.[1] The quantities C, S_A, and D_A, required for second-order calculations, are given in Table IV.

In the limit of large R, the interaction potentials, obtained by the diagonalization of the matrices (17), asymptotically coincide with the interaction potentials obtained in the previous section for Hund's case (c). Using the perturbation treatment,[14] the Eqs. (6) and (13) follow immediately from (17).

Let us demonstrate some of the above-mentioned properties in the case of $\Omega=2$ potentials. From (17a) it follows that the interaction energies are given by

$$\begin{aligned}E_{\pm}=&\tfrac{1}{2}[E_{3/2}(A)+E_{3/2}(B)]+\tfrac{1}{2}[W_1(A)+W_1(B)]R^{-6}\\ &\pm\tfrac{1}{2}(\{E_{3/2}(A)-E_{3/2}(B)+[W_1(A)-W_1(B)]R^{-6}\}^2\\ &\quad+\tfrac{4}{9}C^2R^{-6})^{1/2}\end{aligned}$$

which, for convenience, can be written in shorthand but obvious notation as

$$E_{\pm}=\bar{E}+\bar{W}_1R^{-6}\pm\tfrac{1}{2}[(\Delta E+\Delta W_1R^{-6})^2+\tfrac{4}{9}C^2R^{-6}]^{1/2}\ .$$

In the case of two similar atoms ($A=B$), $\Delta E=0$, $\Delta W_1=0$, and

$$E_{\pm}=\bar{E}\pm\frac{C}{3}R^{-3}+\bar{W}_1R^{-6}\rightarrow\bar{E}\pm\frac{C}{3}R^{-3}\ \text{ as } R\rightarrow\infty\ .$$

For $\Delta E\neq 0$, and R large enough, the following condition is satisfied:

$$(\Delta E+\Delta W_1R^{-6})^2\gg\tfrac{4}{9}C^2R^{-6}$$

and after expanding the square root one finally obtains

$$E_{\pm}=\bar{E}+\bar{W}_1R^{-6}\pm\tfrac{1}{2}(\Delta E+\Delta W_1R^{-6})\pm\frac{C^2}{9\Delta E}R^{-6}\ ,$$

exactly the same results as obtained in Hund's case (c) [see Eqs. (6a) and (13a)].

It is interesting to note that under certain conditions, the interaction potentials in a limited region of internuclear separations R can be dominated by the resonancelike term R^{-3}. If that is the case, the quasistatic wings of the resonance lines would have the van der Waals form followed by the resonance one.[15]

If the condition

$$(\Delta E+\Delta W_1R^{-6})^2\ll\tfrac{4}{9}C^2R^{-6}$$

is satisfied, one can expand the square root in an alternative way obtaining

$$\begin{aligned}E_{\pm}&=\bar{E}+\bar{W}_1R^{-6}\pm\frac{C}{3}R^{-3}\left[1+\frac{9R^6}{8C^2}(\Delta E+\Delta W_1R^{-6})^2\right]\\ &=\bar{E}\pm\frac{C}{3}R^{-3}\left[1+\frac{9(\Delta E)^2}{8C^2}R^6+\frac{9\Delta E\Delta W_1}{4C^2}\right.\\ &\qquad\left.+\frac{9(\Delta W_1)^2}{8C^2}R^{-6}\right]+\bar{W}_1R^{-6}\ .\end{aligned}$$

Now it is easy to see that the required conditions are

$$\max\left[\left[\frac{9(\Delta W_1)^2}{8C^2}\right]^{1/6},\left[\frac{3\bar{W}_1}{C}\right]^{1/3}\right]\ll R\ll\left[\frac{8C^2}{9(\Delta E)^2}\right]^{1/6}.$$

The inclusion of higher-order terms in the energy matrices (17) is straightforward but laborious.

The interaction energies for the K-Rb pair, calculated in the intermediate-coupling region, are shown in Fig. 1. For comparison, the interaction energies calculated for the Hund's case (c) are given by dashed lines. In both cases only the dipole-dipole interaction was taken into account. One can clearly see the effect of mixing of the basis wave functions: In the intermediate-coupling region the overall "repulsion" between "upper" (K*-Rb) and "lower" (K-Rb*) states is weaker than for the pure Hund's case (c). Only the states emerging from the asymptotic K($4S_{1/2}$)-Rb($5P_{1/2}$) level seem to be unchanged.

We have roughly estimated that below $R=12$ Å the higher multipole interactions may influence the interaction energies by more than 10% and furthermore that for $R\leq 10$ Å the exchange contributions become by no means negligible.

V. ABSORPTION COEFFICIENT IN THE WINGS OF RESONANCE LINES

From the diagonalization procedure of the energy matrices (17), not only the interaction energies, but also the coefficients $c_i(R)$ of the basis-set expansion of the corre-

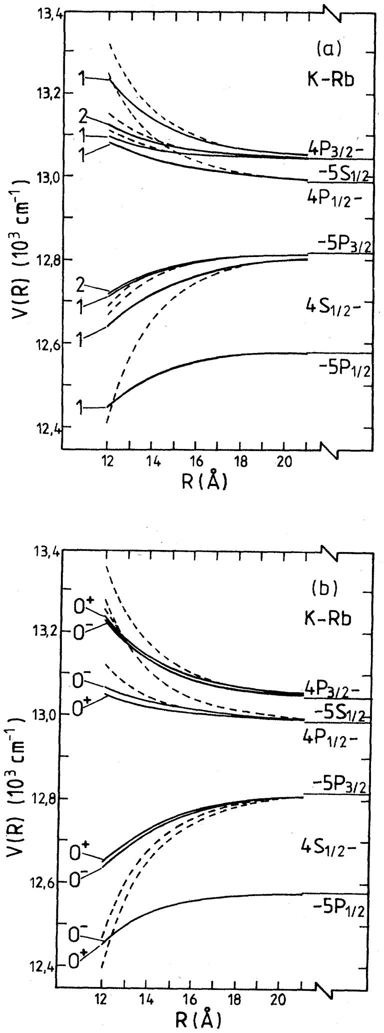

FIG. 1. The interaction energies for the K-Rb pair in the intermediate-coupling region (solid lines) and in the Hund's case (c) (dashed lines); (a) $\Omega=1,2$ potential curves, (b) $\Omega=0^+$, 0^- potential curves.

sponding quasimolecular wave functions can be obtained. It is straightforward to evaluate the relevant molecular absorption oscillator strengths $f(\Omega^{(\pm)})$ for the (vertical) transitions from the ground state(s) $(1,0^{\pm})$ to the excited states $\Omega^{(\pm)}$. The expressions we have obtained are

$$f(2)=\tfrac{1}{6}[c_1^2f_A+c_2^2f_B+2c_1c_2(f_Af_B)^{1/2}]\ , \tag{22a}$$

$$\begin{aligned}f(1)=\tfrac{1}{6}\{&(c_1^2+c_2^2+c_3^2)f_A+(c_4^2+c_5^2+c_6^2)f_B\\&+\tfrac{2}{3}[(\sqrt{2}c_2-c_3)(2c_5-c_6)+\sqrt{3}c_1(c_5+\sqrt{2}c_6)\\&+\sqrt{3}c_4(c_2+\sqrt{2}c_3)](f_Af_B)^{1/2}\}\ ,\end{aligned} \tag{22b}$$

$$\begin{aligned}f(0^+)=\tfrac{1}{12}\{&(c_1^2+c_2^2)f_A+(c_3^2+c_4^2)f_B\\&-\tfrac{2}{3}[c_1c_3-c_2c_4\\&-2\sqrt{2}(c_1c_4+c_2c_3)](f_Af_B)^{1/2}\}\ ,\end{aligned} \tag{22c}$$

$$\begin{aligned}f(0^-)=\tfrac{1}{12}[&(c_1^2+c_2^2)f_A+(c_3^2+c_4^2)f_B\\&+2(c_1c_3+c_2c_4)(f_Af_B)^{1/2}]\ ,\end{aligned} \tag{22d}$$

where f_A and f_B are the total atomic absorption oscillator strengths for the first excited doublet of atoms A and B, respectively $(f=f_{1/2}+f_{3/2})$. [Note that c_i for any particular $f(\Omega)$ means actually $c_i(\Omega;R)$.]

The quasistatic absorption wing profile can be constructed according to the expression[3]

$$k(\omega)=\frac{8\pi^3e^2}{m_ec}N_AN_B\sum_i\frac{f_i(\omega)[R_i(\omega)]^2}{|d\omega/dR_i|}\ . \tag{23}$$

The N_A and N_B are the concentrations of atoms A and B, respectively, the R_i is the root of the equation $\hbar\omega=E_i(R)-E_g(R)$, where $E_i(R)$ is the interaction energy of the ith upper state and $E_g(R)$ is the interaction energy of the ground state, and e, m_e, c, and $\hbar$ have their usual meanings.

In Hund's case (c) the molecular absorption oscillator strengths do not depend on R and are simply proportional to the statistical weights of the corresponding upper states:

$$f(2)=f(1)=2f(0^{\pm})=\tfrac{1}{6}f_A\ . \tag{24}$$

Furthermore, all interaction potentials are of the form $E_i(R)=C_6^{(i)}R^{-6}$ and the quasistatic wing profile is of the form

$$k(\omega)=\frac{4\pi^3e^2}{3m_ec}N_AN_Bf_A\frac{(\Delta C_6^{\mathrm{eff}}/\hbar)^{1/2}}{|\Delta\omega|^{3/2}}\ , \tag{25}$$

where an effective $\Delta C_6^{\mathrm{eff}}$ constant is defined as

$$\Delta C_6^{\mathrm{eff}}=\left[\frac{1}{f_A}\sum_i f_i(\Delta C_6^{(i)})^{1/2}\right]^2 \tag{26}$$

and $\Delta C_6^{(i)}=C_6^{(i)}-C_6^{(g)}$.

The results obtained in Hund's case (c) should be applicable for the case of impact broadening too. The absorption coefficient in the wing of the impact-broadened line is given by[8]

$$k(\omega)=\frac{\pi e^2}{m_ec}N_AN_Bf_A\gamma\,|\Delta\omega|^{-2}\ , \tag{27}$$

where

$$\gamma=8.08v^{3/5}(\Delta C_6^{\mathrm{eff}}/\hbar)^{2/5}\ , \tag{28}$$

$$\Delta C_6^{\mathrm{eff}}=\left[\sum_j\frac{f_i}{f_A}(C_6^{(i)})^{2/5}\right]^{5/2}\ , \tag{29}$$

and v is mean relative velocity of the perturbers.

VI. DISCUSSION AND CONCLUDING REMARKS

The evaluation of the C_6 constants in Hund's case (c) [Eqs. (13)], requires the knowledge of the following parameters: C, S_A, D_A, α, β, γ, and δ, defined by Eqs. (10)–(12) and (15), respectively. The accurate values of C, α, β, γ, and δ follow directly from the oscillator strengths of the first resonance lines and the corresponding energy levels. On the other hand, the evaluation of the radial sums S_A and D_A results in different levels of accuracy due to usually incomplete knowledge of the relevant data. Although the convergence properties of the sums suggest that good results can be obtained from only a few terms, we have further analyzed our values and found out that the combination rules

$$S_{A(B)}S_{B(A)}=S_{A(A)}S_{B(B)}\ ,\qquad D_{A(B)}D_{B(A)}=D_{A(A)}D_{B(B)} \tag{30}$$

($S_{A(B)}$ or $D_{A(B)}$ means that atom A is in the excited state and atom B is in the ground state) are generally satisfied within 2% and in the worst single case (Na-Cs) within 9%. On these grounds we have estimated the values of S_{Rb} and D_{Rb} (see Table II). First, we have taken[8] $S_{\text{Rb(K)}}=S_{\text{K(Rb)}}$ and $D_{\text{Rb(K)}}=D_{\text{K(Rb)}}$, and calculated $S_{\text{Rb(Rb)}}$ and $D_{\text{Rb(Rb)}}$. In the second step we have calculated all other S_{Rb} and D_{Rb}.

From the structure of Eqs. (13) one can see that in the case $\alpha=\beta$ and $\gamma=\delta$ (the fine structure of atom B neglected) the C_6 constants assume only three different values:

$$C_6(\Omega=2,1)=W_1+\frac{C^2}{9\alpha}\ , \tag{31a}$$

$$C_6(\Omega=1,0^{\pm})=W_2+\frac{C^2}{3\alpha} \tag{31b}$$

for the states emerging from the $(n'_AP_{3/2}n'_BS_{1/2})$ asymptotic level, and

$$C_6(\Omega=1,0^{\pm})=W_3+\frac{2C^2}{9\gamma} \tag{31c}$$

for the states emerging from the $(n'_AP_{1/2}n'_BS_{1/2})$ asymptotic level.

This approximation is exactly the same as that used by Kamke *et al.*[4] and from inspection of Table III one can see that it works well in the case of light-alkali-metal-atom perturbers, but not in the case of heavier perturbers, where the fine structure of the perturber's first-excited doublet should be taken into account.

For the calculations in the intermediate-coupling region the coupled basis wave functions were used, i.e., the $|\,nljm\,\rangle$ representation of the atomic wave functions. The uncoupled $|\,nlm_lm_s\,\rangle$ wave functions would, of course, lead to the same results. The uncoupled representation appears to be more convenient for the inclusion of the exchange interaction terms. The spin-orbit interaction is no more diagonal in that representation, but in some cases it can be neglected in the first step of the diagonalization of the effective Hamiltonian, Eq. (1), and *a posteriori* taken into account in an approximate way, if needed.

ACKNOWLEDGMENTS

This work has partial support from the Self-Managing Community of Interest in Science (Socialist Republic of Croatia) and from National Bureau of Standards (Washington, D.C.).

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