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Proposed modification of the criterion for the region of validity of the inverse-power expansion in diatomic long-range potentials

Bing Ji^{a,b,1}, Chin-Chun Tsai^{a,b,2}, William C. Stwalley^{a,b,3}

^a Department of Physics, University of Connecticut, 2152 Hillside Road, U-46, Storrs, CT 06269, USA

^b Institute of Materials Science, University of Connecticut, 2152 Hillside Road, U-46, Storrs, CT 06269, USA

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Abstract

A modified internuclear distance criterion, R_{LR-m} , as the lower bound for the region of validity of the inverse-power expansion of the diatomic long-range potential is proposed. This new criterion takes into account the spatial orientation of the atomic orbitals while retaining the simplicity of the traditional Le Roy radius, R_{LR} for the interaction of S state atoms. Recent experimental and theoretical results for various excited states in Na_2 suggest that this proposed R_{LR-m} is an appropriate generalization of R_{LR} .

1. Introduction

The long-range interaction forces between atoms and molecules are fundamental to the understanding of a great variety of physical phenomena and have attracted much theoretical and experimental attention since the 1960's [1–12]. Among various diverse techniques, diatomic molecular spectroscopy has proven to be a more fruitful and precise way to extract the long-range interactions between two atoms [5,9–12]. In this approach, the long-range portion of

the molecular potential (obtained spectroscopically) is expanded in the inverse-power series,

$$V(R) = - \sum_n \frac{C_n}{R^n}. \quad (1)$$

The coefficients C_n are determined by the nature of the atoms to which the given molecular state dissociates and can be calculated by perturbation theory [1–4,6–8]. An important question that follows is defining the region of validity of this inverse-power expansion. We will examine and answer this question in a quantitative way in this Letter.

Eq. (1) in essence is the multipole expansion of Coulombic interactions between the two separated atoms, which include the electrostatic interactions (present in a first-order perturbation calculation of energy) and the London dispersion forces (the most important second-order perturbations). For Eq. (1) to be valid, the two atoms must be far apart enough so

¹ Also at the Department of Physics and Astronomy, University of Iowa, Iowa City, IA 52242, USA.

² Present address: Department of Physics, University of Texas at Austin, Austin, TX 78712, USA

³ Also at the Department of Chemistry.

that the mutual distortion of their charge clouds is small. As the internuclear distance R decreases, two kinds of forces begin to dominate over the long-range forces: the charge-overlap interaction, i.e. the Coulomb repulsion among the electrons as a direct consequence of the charge cloud overlap; and more importantly, the exchange interaction imposed by the Pauli exclusion principle. Therefore the validity of Eq. (1) requires that these short-range interactions (exchange and charge-overlap terms) must be small compared to the long-range interactions (electrostatic and dispersion terms).

Stwalley and Li first examined this question quantitatively in the long-range analysis of the Mg_2 potential [9,10]. In the Mg_2 case, the inverse-power long-range expansion breaks down badly at $\approx 5 \text{ \AA}$, where the overlap dependent terms are $\approx 15\%$ of the leading $n = 6$ dispersion term. Based on the theoretical long-range analysis of some hydrogen and helium systems [13], Le Roy [11,12] later proposed what is now known as the Le Roy radius R_{LR} as the lower bound of the region in which Eq. (1) is valid (to $\approx 10\%$):

$$R_{\text{LR}} = 2 \left[\langle r^2 \rangle_A^{1/2} + \langle r^2 \rangle_B^{1/2} \right]. \quad (2)$$

Here $\langle r^2 \rangle^{1/2}$ is the r.m.s. distance of the outermost electron. This criterion has been widely adopted in the long-range analysis of various molecular states since then.

Much progress in this field of study has been made since those pioneering works. High resolution all-optical multiple resonance laser spectroscopy [14] using a highly sensitive ionization detector [15] has for the first time reached the long-range near dissociation portions of the potential curves in many excited states in alkali dimers, especially in Na_2 [16–20]. These newly observed spectroscopic data provide direct comparisons with recent theoretical results, such as refined and more reliable long-range calculations which give C_n coefficients of various atomic asymptotes [21,22], and high quality ab initio results which calculate potential curves all the way up to dissociation limits for many electronic states [23,24]. Quantitative examination of these recent results reveals that while the Le Roy radius R_{LR} is a satisfactory criterion for $ns + n's$ atomic asymptotes, it does not provide a realistic lower bound for other asymp-

totates which have atoms with non-zero orbital angular momenta. This is because non-s orbitals are non-spherical and their spatial orientation directly affects the critical R_{LR} internuclear distance. The effect of such spatial orientation is not reflected in Eq. (2). Thus the applicability of R_{LR} is limited primarily to pairs of atoms in s states. In this Letter, we propose a modified criterion for the lower bound of the region of validity of the long-range inverse-power expansion which explicitly takes into account the spatial orientation of atomic orbitals. We will apply this new criterion to some excited states in Na_2 .

It is noteworthy to state at the outset that, in addition to the exchange and charge-overlap corrections, some other types of interactions at long-range (such as pseudo-crossings and ionic-covalent crossings, etc.) may also at times lead to the breakdown of the inverse-power expansion (1). In these cases, diabatic potential curves must first be extracted before the comparison with the long-range expansion can be made. This is analyzed in more details in Refs. [25,26] and is not discussed further here.

2. The m -dependent long-range criterion $R_{\text{LR}-m}$

When two atoms combine together, the orientation of the atomic electronic orbital angular momentum l along the internuclear axis (i.e. the m quantum number along the z axis) determines the electronic angular momentum component Λ of the molecule. As discussed earlier in Section 1, it is the internuclear distance, i.e. the separation of the two atoms *along the internuclear axis*, that determines the competition between the long- and short-range forces. Given that the critical internuclear distance depends not only on the atomic radii, but also on the orientation of the atomic orbitals, i.e. the m quantum numbers of the atomic orbitals, we propose a modified long-range radius that is explicitly m -dependent,

$$R_{\text{LR}-m} = 2\sqrt{3} \left[\langle nlm | z^2 | nlm \rangle_A^{1/2} + \langle n'l'm' | z^2 | n'l'm' \rangle_B^{1/2} \right], \quad (3)$$

where n and n' are the principal quantum numbers; l and l' are quantum numbers of the atomic electronic angular momentum; and m and m' are the components of l and l' on the internuclear axis \hat{z} for the

outermost electrons (i.e. the valence electrons) in atoms A and B, respectively.

Note that

$$z^2 = r^2 \cos^2\theta = \frac{1}{3} \left[\left(\frac{16}{5} \pi \right)^{1/2} Y_{2,0} + 1 \right] r^2. \quad (4)$$

Hence the spacial orientation of the atomic orbitals have been explicitly accounted for in the definition of R_{LR-m} .

To evaluate R_{LR-m} for hydrogenic atoms, we adopt Mizushima's approach [27]⁴ and take the appropriate formulae from Ref. [28]. Specifically, we have

$$\begin{aligned} \langle nlm | z^2 | nlm \rangle &= \left(\frac{1}{3} - \frac{2}{3} \frac{3m^2 - l(l+1)}{(2l+3)(2l-1)} \right) \\ &\times \langle nl | r^2 | nl \rangle. \end{aligned} \quad (5)$$

Note that for n s atomic orbitals, $l = 0$ and $m = 0$, we have

$$\langle z^2 \rangle_{ns} = \frac{1}{3} \langle r^2 \rangle_{ns}, \quad (6)$$

so that R_{LR-m} reduces to the usual R_{LR} when both atoms are in s states.

In general, $\langle nl | r^2 | nl \rangle$ for a hydrogenic atom is given by [29],

$$\langle r^2 \rangle_{nl} = a_\mu^2 \frac{n^4}{Z^2} \left[1 + \frac{3}{2} \left(1 - \frac{l(l+1) - 1/3}{n^2} \right) \right], \quad (7)$$

where Z is the effective nuclear charge and $a_\mu = a_0(m_N/\mu)$. a_0 is the Bohr radius and m_N and μ here are the mass of the nucleus and the reduced mass of the atom, respectively.

For alkali atoms, the principal quantum number n in Eq. (7) must be replaced by the effective principal quantum number n^* ,

$$n^* = n - \alpha(l), \quad (8)$$

where the quantum defect $\alpha(l)$ can be found from standard references [29].

For non-alkali atoms, while Eq. (7) may become rather unreliable, the angular delineation provided by

Table 1

Long-range criteria for various asymptotes in Na_2 . The Greek subscripts denote the m values of the atomic orbitals

Asymptotes	R_{LR-m} (Å)	R_{LR} (Å)
$3s_\sigma + 3s_\sigma$	9.2	9.2
$3s_\sigma + 3p_\sigma$	13.4	11.2
$3s_\sigma + 3p_\pi$	9.7	11.2
$3s_\sigma + 4s_\sigma$	16.5	16.5
$3s_\sigma + 3d_\sigma$	19.4	16.3
$3s_\sigma + 3d_\pi$	17.9	16.3
$3s_\sigma + 3d_\delta$	12.3	16.3
$3s_\sigma + 4p_\sigma$	25.7	20.3
$3s_\sigma + 4p_\pi$	16.8	20.3

Eq. (5) would still be valid under central field approximation in many electron atoms. Values of $\langle |r^2| \rangle_{nl}$ for arbitrary atoms may be readily ob-

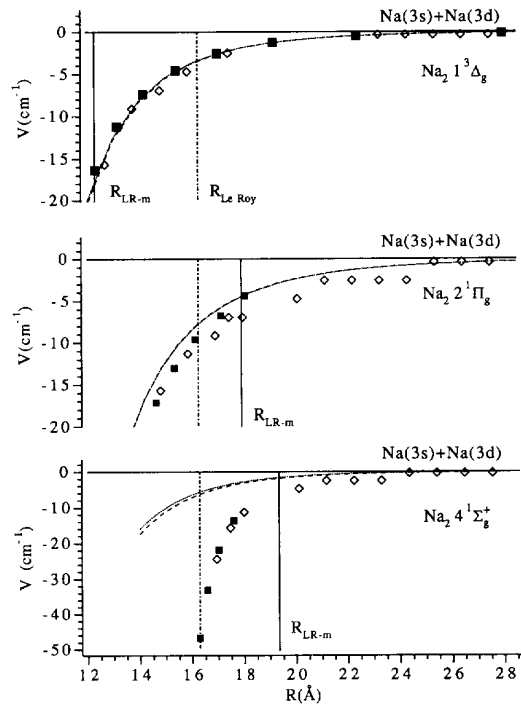


Fig. 1. The long range portions of recent RKR curves (■) which dissociate to $\text{Na}(3s) + \text{Na}(3d)$ limit compared with ab initio calculations from Refs. [23,24] (◇) and long-range C_n coefficients from Refs. [21] (---) and [22] (···). The results of Bussery and Aubert-Frécon and Marinescu and Dalgarno for the $1^3\Delta_g$ and $2^1\Pi_g$ states almost overlap each other on this scale.

⁴ There appears to be a typo in Table 5-3: the factor $(-1)^l$ should be (-1) in the $\beta = 2$, $\gamma = 0$, $l = l'$, and $m = m'$ entry.

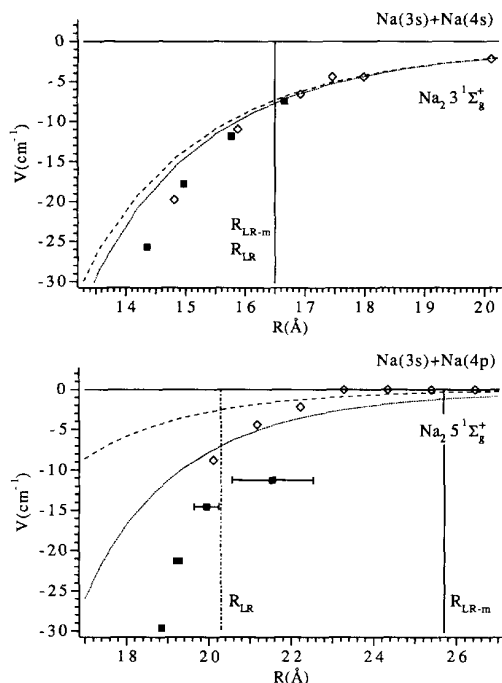


Fig. 2. Same as Fig. 1 but for the dissociation limits Na(3s) + Na(4s) and Na(3s) + Na(4p). RKR curves (■); Refs. [23,24] (◇); Ref. [21] (---); Ref. [22] (···).

tained from standard tables of atomic properties or generated using standard electronic structure computation packages.

3. Application to Na₂ excited states

Table 1 lists the numerical values of R_{LR-m} for various pairs of atomic asymptotes in Na₂, as well as the corresponding values of R_{LR} . To examine the validity of both criteria, long-range portions of the recent experimental RKR potential curves [16–20] together with ab initio calculations [23,24] of five excited states in Na₂ are plotted in Figs. 1 and 2. Also plotted for comparison are the long-range potentials based on the inverse-power expansion Eq. (1) with the C_n coefficients from Bussery and Aubert-Frécon [21] and from Marinescu and Dalgarno [22].

It is evident from these plots that our proposed m -dependent long-range radius R_{LR-m} gives a more

realistic lower bound for the region of validity of the inverse-power expansion for non-S state atoms than the Le Roy radius R_{LR} . This is most dramatically manifested by the Na(3s) + Na(3d) pairs. This is not surprising since the interatomic separation depends more strongly on the atomic orbital orientation for the 3d state than that for ns and np states.

It should also be noted that for the $^1\Sigma_g^+$ states shown in Fig. 1 and 2 (and also $^1\Sigma_u^+$ states), there is significant ion pair character at large internuclear distance and thus R_{LR-m} is probably still not large enough.

4. Conclusion

A modified criterion, namely, the m -dependent radius R_{LR-m} has been proposed as the lower bound for the region of validity of the long-range inverse-power expansion. Application of R_{LR-m} to various excited states of Na₂ demonstrates its superiority compared to the conventional R_{LR} (except for S state atoms where $R_{LR-m} \equiv R_{LR}$). The modified R_{LR-m} has more general applicability while retaining the simplicity of the original R_{LR} . It is expected that this proposed R_{LR-m} will give a more useful guide for use in the long-range analysis of diatomic molecules.

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