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Comment on "Orientation, Alignment, and Hyperfine Effects on Dissociation of Diatomic Molecules to Open Shell Atoms"

Mark D. Havey

Old Dominion University, mhavey@odu.edu

Linda L. Vahala

Old Dominion University, lvahala@odu.edu

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diagonalizing a few-channel Hamiltonian—the energy adaptation may lead to very large reductions in computational effort.

Although the simple approach used here has apparently never been utilized before, it is similar in spirit to other approaches that have been tried. One very similar approach is the method of contracted scattering basis functions, which was developed and applied successfully in the context of the Kohn variational method.³ Another approach that may succeed for the same physical reasons is the use of basis functions based on a semiclassical interpretation of trajectories.⁴ Such basis functions include momentum adaptation and may be more efficient for expanding several degrees of freedom, whereas energy adaptation, which is simpler, should suffice for expanding translational functions in algebraic close coupling approaches¹ to scattering problems. Finally

we note that similar techniques have been employed by Kuruoglu and Micha for expanding the T operator,⁵ and a similar prediagonalization technique has been used by Bačić and Light for discrete-variable ray basis sets for bound-state eigenvalue calculations.⁶

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¹See, for example, D. G. Truhlar, J. Abdallah, Jr., and R. L. Smith, *Adv. Chem. Phys.* **25**, 211 (1974).

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COMMENTS

Comment on "Orientation, alignment, and hyperfine effects on dissociation of diatomic molecules to open shell atoms"

M. D. Havey

Physics Department, Old Dominion University, Norfolk, Virginia 23508

L. L. Vahala

Electrical Engineering Department, Old Dominion University, Norfolk, Virginia 23508

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A recent paper in this journal¹ reported expressions describing the orientation and alignment produced, in an axial recoil limit, by one photon dissociation of diatomic molecules. Reported also were values, applicable to the resonance transitions of the alkali atoms, for orientation and alignment depolarization coefficients $g^{(1)}$ and $g^{(2)}$. However, due to a numerical oversight,¹ most of the values presented for $g^{(k)}$ in that paper are incorrect, in some cases by as much as a factor of 2. We give in this Comment a tabulation of correct $g^{(k)}$ and $g^{(2)}$ values applicable to the resonance transitions of the common alkali isotopes. The values of $g^{(2)}$ we obtain yield linear polarization degrees for the ⁶Li, ⁷Li, and ²³Na resonance transitions in agreement with experimental data.²⁻⁴ Further, due to the dependence of $g^{(k)}$ on measured hyperfine splittings and radiative lifetimes [see Eq. (1) below] there is always some uncertainty in the value of $g^{(k)}$. As estimates of this uncertainty are of considerable value to experimentalists using the $g^{(k)}$, we supplement the values of $g^{(k)}$ presented here with uncertainties in the coefficients derived from those in the measurements. Finally, an application to the results of Rothe *et al.*,⁵ on the polarization of atomic Na D_2 resonance produced in photodissociation of Na₂, is made.

The depolarization coefficients⁶⁻⁸ generally describe the influence of an initially unpolarized and unobserved angular momentum I on an average tensor multipole $\langle T_{kq} \rangle$ describing a state of angular momentum J . The orientation and alignment are the axially symmetric tensors $\langle T_{10} \rangle$ and $\langle T_{20} \rangle$. If a multipole of initial value $\langle T_{kq}(0) \rangle$ becomes depolarized via an interaction between I and J , then $\langle T_{kq} \rangle = g^{(k)} \langle T_{kq}(0) \rangle$, where

$$g^{(k)} = \sum_F \sum_{F'} \frac{(2F'+1)(2F+1)}{2I+1} \frac{W^2(FF'JJ;KI)}{1+(\omega_{FF'}\tau)^2}. \quad (1)$$

Here F and F' are the set of quantum numbers formed by coupling I and J , $W(\dots)$ is a Racah coefficient, and $\omega_{FF'}$ the angular frequency splittings produced by the interaction of I and J . The average duration of the interaction is τ . $\langle T_{kq}(0) \rangle$ might be produced by photodissociation of a diatomic molecule, in an optical collision, or by numerous other excitation mechanisms. Equation (1) is applicable so long as the angular momentum I is not effected by the dynamics of the creation of $\langle T_{kq}(0) \rangle$, and so long as the excitation mechanism is rapid compared to all $\omega_{FF'}$.⁹ If J interacts with more than one angular momentum (say via a fine and hyperfine inter-

TABLE I. A summary of data used to calculate hyperfine depolarization coefficients and values for $g^{(1)}$ and $g^{(2)}$ for common alkali isotopes. Uncertainties in the last digits are given in parentheses; for $g^{(k)}$, if no uncertainty is given, it is less than one-half of the following digit.

Atom	Natural abundance	Nuclear spin	Atomic state	τ (ns)	A (MHz)	B (MHz)	$g^{(1)}$	$g^{(2)}$
⁶ Li	7.5	1	$2^2P_{1/2}$	26.9(2.7)	17.375(18)		0.436(4)	0
			$2^2P_{3/2}$	26.9(2.7)	-1.155(8)	0.10(14)	0.958(5)	0.88(1)
⁷ Li	92.5	3/2	$2^2P_{1/2}$	26.9(2.7)	45.914(25)		0.378	0
			$2^2P_{3/2}$	26.9(2.7)	-3.055(14)	-0.221(29)	0.752(9)	0.49(1)
²³ Na	100	3/2	$3^2P_{1/2}$	16.2(5)	94.3(1)		0.377	0
			$3^2P_{3/2}$	16.1(5)	18.69(9)	2.90(21)	0.555(2)	0.297(1)
³⁹ K	93.3	3/2	$4^2P_{1/2}$	26.2(2.6)	28.85(30)		0.382(1)	0
			$4^2P_{3/2}$	25.8(2.5)	6.06(8)	2.83(13)	0.673(8)	0.372(6)
⁴¹ K	6.7	3/2	$4^2P_{1/2}$	26.2(2.6)	15.19(21)		0.399(3)	0
			$4^2P_{3/2}$	25.8(2.5)	3.40(8)	3.34(24)	0.807(8)	0.55(1)
⁸⁵ Rb	72.2	5/2	$5^2P_{1/2}$	29.4(2.9)	120.72(25)		0.352	0
			$5^2P_{3/2}$	27.0(2.7)	25.009(22)	25.88(3)	0.409(1)	0.237
⁸⁷ Rb	27.8	3/2	$5^2P_{1/2}$	29.4(2.9)	406.2(8)		0.375	0
			$5^2P_{3/2}$	27.0(2.7)	814.845(55)	12.52(9)	0.501	0.270
¹³³ Cs	100	7/2	$6^2P_{1/2}$	34(3.4)	291.90(13)		0.344	0
			$6^2P_{3/2}$	33(3.3)	50.34(6)	-0.38(18)	0.370	0.219

action), Eq. (1) is not applicable; other expressions are available for those cases.⁸

We present in Table I values for $g^{(1)}$ and $g^{(2)}$ for selected excited states of the common alkali isotopes, including those considered by Band *et al.*¹ Also given are the data used to determine the ω_{FF} ; these are largely derived from the recommended values for the dipolar (A) and quadrupolar (B) coupling constants (and their uncertainties) as tabulated by Arimondo *et al.*^{10,11} Radiative lifetimes were taken from summaries of atomic transition probabilities.^{12,13} The quoted uncertainties in $g^{(k)}$ were obtained by assuming that the given uncertainties in A , B , and τ are statistical, and represent one standard deviation. Equation (1) was then used to calculate¹⁴ the uncertainty in $g^{(k)}$.

As an example of the utility of these results, consider the experiment on the photodissociation of Na₂ by Rothe *et al.*,⁵ via the $B^1\Pi_u-X^1\Sigma_g^+$ transition.¹⁵ Photodissociation of Na₂ at 457.9 nm produced mainly atomic Na in the $3p^2P_{3/2}$ fine-structure level. The resulting atomic Na $3p^2P_{3/2}-3s^2S_{1/2}$ resonance fluorescence was observed at right angles to the exciting light and its polarization vector, and was observed to have a linear polarization degree P_L of $-5(1)\%$; $P_L = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$. In terms of the alignment, and for the geometry of the experiment⁷

$$P_L = \frac{3h^{(2)} \langle T_{20} \rangle}{4 + h^{(2)} \langle T_{20} \rangle}, \quad (2)$$

where $h^{(2)}$ is a ratio of Racah coefficients and is characteristic of the angular momentum of the initial and final states. For a $2^2P_{3/2}-2^2S_{1/2}$ transition $h^{(2)}$ has a value of $-5/4$. Using the

results of Table I with $\langle T_{20} \rangle = 0.053(11)$, we have $\langle T_{20} \rangle = \langle T_{20} \rangle / g^{(2)} = 0.18(4)$. Thus a proper analysis of this Na₂ photodissociation process, with the obscuring effects of the atomic Na hyperfine structure accounted for, must consider an alignment of $0.18(4)$. This value would produce a linear polarization degree of about $-18(4)\%$ in the absence of hyperfine structure.

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