Is photon angular momentum important in molecular collision processes occurring in a laser field?

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The importance of the rigorous treatment of photon angular momentum in molecular-collision processes occurring in the presence of intense radiation is investigated. An alternate approximate treatment, which essentially neglects the angular momentum coupling between the photon and the molecular degrees of freedom by averaging over the angular dependence of the interaction matrix elements, is presented and applied to a model calculation. The degeneracy-averaged results of this calculation compare remarkably well with the results of a rigorous calculation, from which we conclude (with reservation) that the explicit consideration of photon angular momentum coupling in molecular-collision problems is unnecessary.

I. INTRODUCTION

Recently,[1] the quenching of fluorine by xenon in the presence of intense radiation from the KrF laser was investigated. Since this was the first calculation of its sort, the collision dynamics and, in particular, the angular momentum of the photon, were treated in a simplified manner. (We hasten to add that the calculation as performed was far from trivial. Only through the use of such simplifications was the problem computationally tractable.) The proper treatment has been derived[2] within a close-coupled equations formalism, although the resulting system of equations is somewhat complex and constitutes a far more difficult (and time consuming) numerical problem than the corresponding field-free one. In this Comment we discuss, in terms of numerical solutions of a model problem, the importance of these additional complications and hence the importance of rigorous, explicit consideration of photon angular momentum in molecular- (atom-atom) collision problems.

In Sec. II, we discuss the nature of the complications involved in the full treatment of photon angular momentum. The matrix element of the interaction Hamiltonian and an alternate treatment of photon angular momentum are discussed in Sec. III. The model calculation is described and our results reported in Sec. IV. In Sec. V, our conclusion concerning the importance of photon angular momentum in collisional problems is presented.

II. NATURE OF THE COMPLICATIONS

Before discussing the complications arising in rigorously describing molecular collisions in a field, let us review the description of molecular collisions in the absence of a field. The states used to describe such a collision are usually indexed by eigenvalues of the total angular momentum J and its space-fixed projection M. Due to rotational invariance of the Hamiltonian, J and M conserved. The only allowed transitions are thus within the JM sets, i.e., transitions from a state in the set JM to a state in the set $J'M'$, $J \neq J'$ or $M \neq M'$, are forbidden. Furthermore, the close-coupled equations show no dependence on M so that the probability for the transition $\alpha \rightarrow \beta$ in the set JM is exactly the same as for the $\alpha \rightarrow \beta$ transition in the set JM'. This equivalence is used to advantage in the derivation of the degeneracy-averaged cross section and gives rise to the $2J+1$ factor in the usual expression.

Now consider the complications arising from the field. The states used to describe the system are a direct product of the field-free states, indexed by J and M, and the states of the radiation field. For simplicity, we will assume that the field is single mode (which we represent by an occupation-number state), and interacts with matter only through the dipole operator. An appropriate set is then indexed by J, M, and n, but none of these need be conserved in a radiative transition since the system as a whole is no longer rotationally invariant. Consider the transition from a state in the set of JMn to a state in the set $J'M'n'$ by absorption of a photon. Since there is now one less photon in the field, n' is given as $n' = n - 1$. The projection M' is simply the sum of the initial projection M and the projection of the photon angular momentum σ which is merely the photon polarization expressed in spherical coordinates. The final total angular momentum $\vec{J}$ is obtained from the vectorial combination of the initial angular momentum $\vec{J}$ and the photon angular momentum, so that J' satisfies the inequality $|J-1| \leq J' \leq J+1$. To be fully general, we should also consider the next

level of complexity, a subsequent photon absorption to a state in the set $J''M''n''$. But even without doing so, the complexity of the problem is obvious. The dimensionality of the problem has been considerably increased (over the field-free one), and since the difficulty of a numerical solution goes as N^3, this is of considerable concern. But of even greater concern is that the system is no longer rotationally invariant, so that the close-coupled equations are no longer independent of M. Thus each set of equations indexed by initial M must be solved independently, i.e., the summation giving rise to the $2J+1$ factor in the field-free degeneracy-averaged cross section cannot be performed analytically, but must be performed numerically. (Actually, symmetry considerations decrease the number of independent M's by one-half, but this hardly compares to the $2J+1$ reduction in the field-free case.)

III. INTERACTION MATRIX ELEMENT

The complexities discussed in the previous section all arise from the matrix element of the interaction Hamiltonian,

$$H^{\text{int}} = H_0^{\text{int}} \sum_j (a_\sigma \nabla_{j\sigma} + a_\sigma^\dagger \nabla_{j\sigma}^*) , \tag{1}$$

where H_0^{int} is a collection of the appropriate constants, a_σ and $a_\sigma^\dagger$ are annihilation and creation operators for the photon number state $|n_\sigma\rangle$, $\nabla_{j\sigma}$ is the σth component of $\vec{\nabla}_j$ (in the space-fixed coordinate system), and the j summation is over all electrons. (For convenience, we henceforth define $\nabla_\sigma \equiv \sum_j \nabla_{j\sigma}$.) We denote by $|j\Omega\rangle$ a body-fixed diabatic basis for the electronic plus spin-orbit Hamiltonian which is an eigenfunction of $\vec{j}$ (the sum of all electronic orbital angular momenta and spins) and $\vec{j}_{z'}$ (the projection of $\vec{j}$ on the internuclear axis). A field-free total angular momentum wave function can then be written as

$$|JMj\Omega\rangle = \left(\frac{2J+1}{4\pi}\right)^{1/2} D^J_{\Omega M}(0, -\theta, -\phi)\,|j\Omega\rangle , \tag{2}$$

so that the matrix elements of interest are of the form

$$\begin{aligned}\langle n'_\sigma|\langle J'M'j'\Omega'|H_0^{\text{int}} a_\sigma \nabla_\sigma|JMj\Omega\rangle|n_\sigma\rangle &= H_0^{\text{int}}\langle n'_\sigma|a_\sigma|n_\sigma\rangle\langle J'M'j'\Omega'|\nabla_\sigma|JMj\Omega\rangle \\ &= H_0^{\text{int}}(n_\sigma)^{1/2}\delta(n'_\sigma, n_\sigma - 1) \\ &\quad \times \langle J'M'j'\Omega'|\nabla_\sigma|JMj\Omega\rangle ,\end{aligned} \tag{3}$$

and a corresponding matrix element for $a_\sigma^\dagger \nabla_\sigma^*$. Relating ∇_σ to its body-fixed components, the matrix element of ∇_σ can be written as

$$\begin{aligned}&\langle J'M'j'\Omega'|\nabla_\sigma|JMj\Omega\rangle \\ &\quad = \langle J'M'j'\Omega'|\sum_\eta D^1_{\eta\sigma}\nabla_\eta|JMj\Omega\rangle \\ &\quad = \frac{[(2J+1)(2J'+1)]^{1/2}}{4\pi}\sum_\eta \int D^{J'*}_{\Omega'M'} D^1_{\eta\sigma} D^J_{\Omega M}\, d\hat{R} \\ &\qquad\qquad \times \langle j'\Omega'|\nabla_\eta|j\Omega\rangle \\ &\quad = \left[\frac{[(2J+1)(2J'+1)]^{1/2}}{4\pi}\int D^{J'*}_{\Omega'M'} D^1_{\Omega'-\Omega,\sigma} D^J_{\Omega M}\, d\hat{R}\right] \\ &\qquad \times \delta(M', M+\sigma)\langle j'\Omega'|\nabla_{\Omega'-\Omega}|j\Omega\rangle \\ &\quad = \left[\left(\frac{2J+1}{2J'+1}\right)^{1/2} C(J1J'; \Omega, \Omega'-\Omega) C(J1J'; M, \sigma)\right] \\ &\qquad \times \delta(M', M+\sigma)\langle j'\Omega'|\nabla_{\Omega'-\Omega}|j\Omega\rangle .\end{aligned} \tag{4}$$

It should be clear that all the complexities that we have discussed stem from quantities such as that contained in the square brackets of Eq. (4).

To assess the importance of these complexities, it is necessary to compare the results of the full treatment, as in Eq. (4), with those of another treatment which in some sense ignores photon angular momentum. The alternate treatment chosen for discussion in this Comment consists of the replacement of the square bracket in Eq. (4) by a simpler form. First, $C(J1J'; M\sigma)$ is replaced by its root-mean-square average $\bar{C}_M$:

$$\bar{C}_M = \left(\frac{1}{2J+1}\sum_M C(J1J'; M\sigma)^2\right)^{1/2} = \frac{1}{\sqrt{3}}\left(\frac{2J'+1}{2J+1}\right)^{1/2} . \tag{5}$$

By introducing this average we have essentially imposed rotational invariance upon the system (e.g., the M quantum number no longer appears in any of the matrix elements). The remaining Clebsch-Gordon coefficient could be replaced in a similar manner, but this would not lead to any simplifications. Rather, we shall truncate the basis to include only those states with $J' = J$, but include in the interaction matrix element the effect of the interactions to all J' states by replacing the Clebsch-Gordon coefficient by its root-sum-square $\bar{C}_{J'}$:

$$\bar{C}_{J'} = \left(\sum_{J'} C(J1J'; \Omega, \Omega'-\Omega)^2\right)^{1/2} = 1 . \tag{6}$$

(In making these averaging approximations, we recognize that we have discarded certain parity information in the original Clebsch-Gordon coefficients.) Thus Eq. (4) becomes

$$\begin{aligned}\langle J'M'j'\Omega'|\nabla_\sigma|JMj\Omega\rangle &= \delta(J, J')\delta(M', M+\sigma) \\ &\quad \times (\mathcal{P}/\sqrt{3})\langle j'\Omega'|\nabla_{\Omega'-\Omega}|j\Omega\rangle ,\end{aligned} \tag{7}$$

where $\mathcal{P}$, a quantity having unit modulus, has been introduced to preserve the correct parity of the matrix element. In the actual calculation a parity basis is introduced which simplifies both the full and the alternate treatments. The close-coupled equations, with appropriate scattering boundary conditions, can then be solved by the standard methods leading to transition probabilities and cross sections. We note that, since our alternate treatment was derived by an averaging procedure, it would be inappropriate not to average the final results. Hence only degeneracy-averaged cross sections will be reported in this Comment.

IV. MODEL CALCULATION

To perform a comparison of the two treatments, a model system was chosen for numerical calculations. Although this model does not represent any specific physical system, it mimics the collision of a halogen with a rare-gas atom, i.e., a ^2P-state atom colliding with a ^1S-state atom. The various parameters appearing in the model were chosen purely for convenience. The electronic states arising in such a collision are of Σ and Π symmetry, and for these potentials we chose (in a. u.)

$$V(\Sigma,R)=\exp[-3(R-2.5)],$$
$$V(\Pi^{\pm},R)=\exp[-1.5(R-2.5)]. \tag{8}$$

Note that a superscript has been added to Π to distinguish between the two degenerate states. We chose the dipole moment to be a Gaussian function peaked at 6 bohrs, with a maximum value of 2 a.u. After making the appropriate conversion of units and introducing the field intensity (in W/cm^2), the interaction matrix element is given in a.u. as

$$H_0^{\rm int}\langle n_\sigma|a_\sigma|n_\sigma+1\rangle\langle\Pi^{\pm},R|\nabla_{\pm}|\Sigma,R\rangle = 5.34\times10^{-9}\sqrt{I}\exp[-(R-6)^2]. \tag{9}$$

The radiation field is provided by the 10.6-μm line of the CO_2 laser with a photon energy of 0.0043 hartree. The ^2P-state atom was chosen to have a spin-orbit splitting of 0.002 hartree, and the reduced mass of the system was taken to be 2500. These parameters, together with the intensity of the field, suffice to define the model system.

The transition of interest is the quenching process $^2P_{1/2}\rightarrow{}^2P_{3/2}$ (for a halogen the $^2P_{1/2}$ state lies at a higher energy than the $^2P_{3/2}$ state). Rather than the $|JMj\Omega\rangle$ basis, the parity basis $|JMj|\Omega|\epsilon\rangle$ is actually used in the calculations. For nonradiative processes, only transitions between states of the same parity are allowed, while a change of parity accompanies a radiative transition. This parity selection reduces the number of states to be considered simultaneously, and hence reduces the difficulty of the problem. In this Comment, we consider only those states coupled to the even-parity state correlating to $^2P_{1/2}$, $|JM,\frac{1}{2},|\frac{1}{2}|,\epsilon=1\rangle|n_\sigma\rangle$. This state is coupled to the states

$$|JM,\tfrac{3}{2},|\tfrac{1}{2}|,\epsilon=1\rangle|n_\sigma\rangle,$$
$$|JM,\tfrac{3}{2},|\tfrac{3}{2}|,\epsilon=1\rangle|n_\sigma\rangle \tag{10}$$

by nonradiative coupling and, in the full treatment of photon angular momentum, to the states

$$\begin{aligned}&|J+1,M-\sigma,\tfrac{3}{2},|\tfrac{1}{2}|,\epsilon=-1\rangle|n_\sigma+1\rangle,\\ &|J+1,M-\sigma,\tfrac{3}{2},|\tfrac{3}{2}|,\epsilon=-1\rangle|n_\sigma+1\rangle,\\ &|J,M-\sigma,\tfrac{3}{2},|\tfrac{1}{2}|,\epsilon=-1\rangle|n_\sigma+1\rangle,\\ &|J,M-\sigma,\tfrac{3}{2},|\tfrac{3}{2}|,\epsilon=-1\rangle|n_\sigma+1\rangle,\\ &|J-1,M-\sigma,\tfrac{3}{2},|\tfrac{1}{2}|,\epsilon=-1\rangle|n_\sigma+1\rangle,\\ &|J-1,M-\sigma,\tfrac{3}{2},|\tfrac{3}{2}|,\epsilon=-1\rangle|n_\sigma+1\rangle\end{aligned} \tag{11}$$

by radiative coupling. From our discussion in Sec. II we see that this nine-state problem must be solved repeatedly for various M's, and the sum over M (in the degeneracy-averaged cross section) must be performed numerically. Some savings in effort is realized by recognizing that for linearly polarized radiation $\sigma=0$, the transition probabilities for $-M$ are the same as for $+M$, and so only the positive M's need be numerically considered. (An analogous situation exists for circularly polarized light.) In our alternate approximate treatment of photon angular momentum, the state $|JM,\frac{1}{2},|\frac{1}{2}|,\epsilon=1\rangle|n_\sigma\rangle$ is radiatively coupled to the states

$$|J,M-\sigma,\tfrac{3}{2},|\tfrac{1}{2}|,\epsilon=-1\rangle|n_\sigma+1\rangle \tag{12}$$

and

$$|J,M-\sigma,\tfrac{3}{2},|\tfrac{3}{2}|,\epsilon=-1\rangle|n_\sigma+1\rangle. \tag{13}$$

However, the potential curve for the second state never approaches the potential curve for the initial state, so that it should not contribute significantly to the quenching process. This state will be excluded in our calculations. Furthermore, although the initial state is collisionally coupled to both states of Eq. (10), we assume that $|\Omega|$ is conserved in these nonradiative transitions and will include only the state

$$|JM,\tfrac{3}{2},|\tfrac{1}{2}|,\epsilon=1\rangle|n_\sigma\rangle \tag{14}$$

in our calculations.

It should be clear that our alternate treatment of photon angular momentum in this collision problem is considerably less complicated than the full treatment. This will be dramatically shown by a comparison of computational times required

TABLE I. Partial cross sections for quenching by linearly polarized 10.6-μm light.

Field (w/cm^2)	J	Collision energy (eV)	Cross sections (Å^2) Exact[a]	Approximate[b]	Approximate[c]
0	$\frac{7}{2}$	0.1	0.3329(−1)	0.3335(−1)	
		0.2	0.6890(−2)	0.6380(−2)	
	$\frac{23}{2}$	0.1	0.7287(−2)	0.2597(−2)	
		0.2	0.8716(−1)	0.8521(−1)	
10^9	$\frac{7}{2}$	0.1	0.4202(−1)	0.4159(−1)	0.4153(−1)
		0.2	0.7523(−2)	0.7271(−2)	0.7781(−2)
	$\frac{23}{2}$	0.1	0.2089(−1)	0.1502(−1)	0.1971(−1)
		0.2	0.9494(−1)	0.9214(−1)	0.9409(−1)
10^{10}	$\frac{7}{2}$	0.1	0.1085	0.1077	0.1076
		0.2	0.1469(−1)	0.1449(−1)	0.1499(−1)
	$\frac{23}{2}$	0.1	0.1312	0.1177	0.1224
		0.2	0.1450	0.1433	0.1452

[a] Exact nine-state results, numerically summed.
[b] Approximate three-state results.
[c] Approximate three-state results, modified by the additions of the difference of the field-free cross sections.

for solution. In fact, the full treatment is sufficiently time consuming so that we shall present partial cross sections (degeneracy-averaged) at only two collisional energies and at two (nonzero) field intensities. The results for quenching in the presence of the radiation field, presented in Table I, indicate that the alternate treatment does surprisingly well. Only for $J=\frac{23}{2}$ at the lower collision energy is there a discrepancy of more than 4% in the cross section. Our results can be improved with trivial effort if we ascribe this discrepancy to the fact that a collisionally coupled state was ignored in the approximate treatment. Assuming that the ignored state represents a totally independent channel (unaffected by the presence of the field), its contribution to the cross section is simply the difference between the exact and approximate results at zero-field intensity. Adding this contribution to the approximate cross sections, the values exhibited in the last column of Table I were obtained. None of these cross sections are in error by more than 7%.

This remarkable agreement is even more surprising when we consider the computational time required. (Our algorithm, based upon the R-matrix method of Light and Walker,[3] is divided into preparatory and actual scattering calculations. The time required for preparation represents an "overhead" which should be averaged over the number of collision energies used, so that the average time for a calculation is dependent upon the number of calculations performed. Thus we will exclude the preparation time, and only report the average time required for the actual scattering portion of the calculation. Since the same step-size parameters were used for both the full and approximate treatments, a valid comparison of times can be made.) For the $J=\frac{7}{2}$ calculations, the full treatment required 28 times more effort than the approximate treatment. The full treatment for $J=\frac{23}{2}$, requiring solutions of the nine-state problem for all 12 positive M's, required 81 times the effort of the approximate treatment. To compute all the cross sections through $J=\frac{23}{2}$, almost 100 times more effort would be required for the full treatment of photon angular momentum as compared to the approximate treatment. Furthermore, it appears from the values in Table I that this would not be sufficient to obtain converged total cross sections.

V. CONCLUSION

From the results of Sec. IV, it is apparent that cross sections in error by only a few percent can be obtained with orders-of-magnitude less effort than required by a full treatment of photon angular momentum. With certain reservations, we conclude that the explicit consideration of the angular momentum coupling between the photon and the molecular degrees of freedom in collision problems is unnecessary. Our reservations pertain to the fact that this conclusion is based upon a very limited number of calculations. It is quite possible that our approximate formalism would not perform as well on some other collision system, or at different collision energies and field intensities. In particular, it is expected that at very high intensities, alignment effects of the colliding system due to the radiation field

would become important and invalidate our averaging approximations. However, that a formalism as crude as the one we have presented should work at all tends to lend support to our conclusion, and we suspect that a more sophisticated treatment might be more generally applicable while still avoiding the shortcomings of the full treatment of photon angular momentum in collision problems.

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[1]P. L. DeVries, M. S. Mahlab, and T. F. George, Phys. Rev. A. 17, 546 (1978).

[2]P. L. DeVries and T. F. George, Mol. Phys. 36, 151 (1978).

[3]J. C. Light and R. B. Walker, J. Chem. Phys. 65, 4272 (1976).