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CHANGE OF ATOMIC SPINS IN SLOW COLLISIONS

A. P. Blinov

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In the present work, slow atomic collisions with changes of atomic spins are examined. In this case, the electron spin exchange in the process of collisions causes the polarization characteristics of atoms to change. Formalism has been constructed based on the adiabatic approximation and polarization operator technique for a description of changes of arbitrary spins of colliding atoms. Singlet-triplet transitions, analogous to those of inelastic exchange electron scattering on two-electron atoms, are described for collisions of hydrogen and alkali metal (H, K, Na, Cs, *and* Rb) *atoms with two-electron atoms or ions* (He, Li^+, *and* Hg). *The processes of the type* $H(^2S) + He(^1S) \to H(^2S) + He(^3S)$ *and* $P\left(^4S_{3/2}\right) + He\left(^3S_1\right) \to P\left(^2S_{1/2}\right) + He\left(^3S_1\right)$ *are also considered.*

INTRODUCTION

The spin exchange effects in slow collisions of two atoms with valence *S*-electrons (H, K, Na, Cs, and Rb) that occur by the scheme

$$A\uparrow + B\downarrow \to A\downarrow + B\uparrow , \tag{1}$$

where arrows indicate the direction of spins of colliding atoms *A* and *B*, were studied in [1].

In the present paper, it is assumed that in processes (1) atoms *A* and *B* have arbitrary spins S_1 and S_2, and the spin exchange in a wider sense involves changes of not only orientations, but also atomic spin magnitudes as a result of collision.

CONSTRUCTION OF FORMALISM FOR A DESCRIPTION OF SPIN EXCHANGE

Spin exchange (1) is analogous to resonant charge transfer [2]. Exactly the $A + B$ system can be considered as a quasi-molecule with different electronic terms – energy levels $E^S_{S_1,S_2}(R)$ – depending on the internuclear distance R, where *S* is the total spin of the $A + B$ system and $|S_1 - S_2| \le S \le S_1 + S_2$.

Let $\psi_1{}^{S_1M_1}$ and $\psi_2{}^{S_2M_2}$ be wave functions of the initial states of colliding particles. According to perturbation theory, when the internuclear distance R changes with time, the nonstationary wave function of the system at time *t* is equal to

$$\Psi = \sum_{SM} \sum_{\substack{S_1' M_1' \\ S_2' M_2'}} C^{SM}_{S_1' M_1' S_2' M_2'} C^{SM}_{S_1M_1S_2M_2} \psi_1^{S_1' M_1'} \psi_2^{S_2' M_2'} \exp\left[-i \int_{-\infty}^{t} E^S_{S_1', S_2'}\, dt'\right], \tag{2}$$

where $\Psi(t = -\infty) = \psi_1{}^{S_1M_1}\psi_2{}^{S_2M_2}$ and $C^{SM}_{S_1M_1S_2M_2}$ are the Clebsch–Gordan coefficients [3].

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In this case, to describe the collision pattern, it is convenient to introduce a matrix $\hat{a}$ whose rows are numbered in accordance with pairs of the initial values (M_1, M_2) and columns are numbered in accordance with pairs of final values (M_1', M_2') of spin projections for atoms *A* and *B*.

In the adiabatic approximation, the probability of elementary collision act $A(S_1, M_{1)}) + B(S_2, M_2) \rightarrow A(S_1', M_1') + B(S_2', M_2')$ accompanied by changes of spin states is equal to

$$W_{M_1 M_2}^{M_1' M_2'}(r) \equiv \left| a_{M_1 M_2}^{M_1' M_2'} \right|^2 = \left| \left\langle \psi_1^{S_1' M_1'} \psi_2^{S_2' M_2'} \left| \Psi(t=\infty) \right\rangle \right|^2 . \tag{3}$$

The collision cross section is equal to

$$Q_{M_1 M_2}^{M_1' M_2'} = \int_0^\infty 2\pi r\, dr \left| a_{M_1 M_2}^{M_1' M_2'} \right|^2 (r), \tag{4}$$

where *r* is the impact parameter of collision.

If all possible spin orientations of atoms before and after collision of atoms *A* and *B* have been taken into account, of practical interest is the probability $\tilde{W}$ and the collision cross section $\tilde{Q}$ averaged over the projections of particle spins in the initial state and summed over the spin projections in the final state. In addition, the polarization characteristics of atoms also change.

Averaging of Eq. (4) over M_1, M_2 and summation over M_1', M_2', invoking the initial spin density matrix ρ [3, 4] of the *A* + *B* system, gives

$$\tilde{W} = \mathrm{Sp}(\hat{a}\rho\hat{a}^+), \; \tilde{Q} = \int_0^\infty 2\pi\, r\, dr \tilde{W}(r) \tag{5}$$

(here Sp denotes the sum of diagonal matrix elements). The spin characteristics after collision can be found by the standard method [3, 4]. Thus, spin polarizations $\boldsymbol{P}_1'$ and $\boldsymbol{P}_2'$ after collision of atoms *A* and *B* assume the form

$$\boldsymbol{P}_\lambda' = \frac{\mathrm{Sp}\left(\hat{a}\rho\hat{a}^+ \hat{\boldsymbol{S}}_\lambda'\right)}{\tilde{W}}, \tag{6}$$

where $\boldsymbol{S}_\lambda'$ denotes the spin operators S_1' and S_2' after collision.

In the absence of relativistic interactions, when the spin *S* of the system of colliding particles remains unchanged, the matrix $\hat{a}$ is reconstructed as follows:

$$\hat{a} = \sum_S A_S\left(S_1', S_2'\right)\hat{\Pi}_S\left(S_1, S_2; S_1', S_2'\right), \tag{7}$$

where the elements of matrices $\hat{\Pi}_S$ are

$$\Pi_{S M_1 M_2}^{M_1' M_2'} = \sum_{\substack{M_S = M_1 + M_2 = \\ = M_1' + M_2'}} C_{S_1 M_1 S_2 M_2}^{S M_S} C_{S_1' M_1' S_2' M_2'}^{S M_S} . \tag{8}$$

In Eq. (8), $C_{S_1 M_1 S_2 M_2}^{S M_S}$ are the Clebsch–Gordan coefficients, and the coefficients A_S in Eq. (7) are equal to

$$A_S\left(S_1',\,S_2'\right)=\frac{1}{N}\left[\exp\left(-i\int\limits_{-\infty}^{+\infty}E^S_{S_1',S_2'}\,dt\right)\right], \tag{9}$$

where $E^S_{S_1',S_2'}$ are the corresponding terms of the $A\left(S_1'\right)B\left(S_2'\right)$ quasi-molecule incorporating the atoms in the final state, and $N=S_1+S_2+1-\left|S_1-S_2\right|$ is the number of collision channels corresponding to different values of the total spin S of two atoms in the initial state. We note that identical nuclei A and B possess permutation symmetry. This results in even g- and odd u-states of the AB quasi-molecule (in particular, the AA quasi-molecule) and in the corresponding terms E_g or E_u. An analysis demonstrates that by analogy with the resonant charge transfer [5], the coefficients A_S in this case must be set equal to $A_S=\frac{1}{2N}\left[\exp\left(-i\int\limits_{-\infty}^{+\infty}E^S_g\,dt\right)-\exp\left(-i\int\limits_{-\infty}^{+\infty}E^S_u\,dt\right)\right]$, where $E^S_{g,u}$ are the corresponding terms of the AB quasi-molecule. It should also be emphasized that in general, the matrix $\hat{a}$ is rectangular (the number of its rows differs from the number of its columns).

It is convenient to carry out calculations by formulas (5) and (6) with the help of the polarization operators $\hat{T}_{LM}(S)$ whose matrix elements are expressed in terms of the Clebsch–Gordan coefficients [3]:

$$\left[\hat{T}_{LM}(S)\right]_{\sigma\sigma'}=\sqrt{\frac{2L+1}{2S+1}}C^{S\sigma'}_{S\sigma LM} \tag{10}$$

$$\left(\sigma,\sigma'=-S,-S+1,...,S\right).$$

An arbitrary $(2S+1)\times(2S+1)$ matrix can be expanded in the complete system of polarization matrices $\hat{T}_{LM}(S)$:

$$\hat{A}=\sum_{L=0}^{2S}\sum_{M=-L}^{L}(-1)^M t_{L-M}\hat{T}_{LM}, \tag{11}$$

where the expansion coefficients are equal to

$$t_{LM}=\mathrm{Sp}\left(\hat{A}\hat{T}_{LM}\right). \tag{12}$$

The initial spin density matrices ρ_A and ρ_B of atoms A and B can be expanded in the polarization operators, where the corresponding polarization moments contain information about the initial preparation of colliding atoms. In the cyclic basis, for example, we have

$$t^{A,B}_{1-M}=(-1)^M\frac{\sqrt{2}}{2}P^{A,B}_{-M}, \tag{13}$$

where the covariant components are $P_0=P_z$ and $P_{\pm1}=\mp\frac{1}{2}\left(P_x\pm iP_y\right)$.

For independent preparation of the states of colliding atoms, the initial density matrix of the $A+B$ system is

$$\rho^{AB}=\rho_1\otimes\rho_2, \tag{14}$$

where $\otimes$ denotes a direct matrix product.

Calculations of the concrete parameters in the examined approach with the use of the polarization operators are reduced to finding sums of products of the corresponding Clebsch–Gordan coefficients [3].

RESULTS AND THEIR DISCUSSION

Let us consider first the processes of the following form:

$$A\left(S_1 = 1/2\right) + B\left(S_2 = 0\right) \to A\left(S_1' = 1/2\right) + B\left(S_2' = 1\right). \tag{15}$$

In this case, the singlet-triplet transition of atom B occurs after collision with atom A [for example, in the process $\mathrm{H+He}(^1S) \to \mathrm{H+He}(^3S)$].

Application of formalism (5)–(14) under condition that the initial density matrices are

$$\rho_1 = \frac{1}{2}\left[I + \sum_i P_{1i}\hat{\boldsymbol{\sigma}}_{1i} \right], \quad \rho_2 = 1, \tag{16}$$

where ($i = x, y, z$), yields the following results.

The probability of collision with changes of the spin states ($N = 2$) is

$$\tilde{W} = \left| A_{1/2}\left(\tfrac{1}{2}, 1\right) \right|^2 = \frac{1}{4}. \tag{17}$$

Polarization of atoms after collision as the result of the singlet-triplet transition of atom B is

$$\boldsymbol{P}_1' = -\frac{1}{3}\boldsymbol{P}_1, \; \boldsymbol{P}_2' = \frac{2}{3}\boldsymbol{P}_1. \tag{18}$$

Results (17) and (18) are reduced to those obtained in [4] for inelastic exchange scattering of electrons by two-electron atoms in the LS-bond approximation. On the other hand, as pointed out in [4], the LS-bond approximation can be insufficient for a description of a heavy atom. Thus, the electron depolarization $D = P_1' / P_1$ differs from –1/3 and is a complex function of the collision energy when the $^1S \to {}^3P$ transition is excited by electrons in the mercury atom. Therefore, the description of collisions of heavy atoms accompanied by changes of their spins can deviate from the scheme of the pure LS-bond.

Let us consider now the processes with $S_1 = 3/2, \; S_2 = 1 \to S_2' = 1/2$, and $S_2' = 1$. An example of this process is collision of phosphor atoms with a metastable helium atom:

$$\mathrm{P}\left({}^4S_{3/2} \right) + \mathrm{He}\left({}^3S_1 \right) \to \mathrm{P}\left({}^2S_{1/2} \right) + \mathrm{He}\left({}^3S_1 \right). \tag{19}$$

The metastable helium atoms $\mathrm{He}\left({}^3S_1 \right)$ are considered to be polarized before collision, which can be realized, for example, by extraction of the helium atoms from the plasma exposed to optical pumping by circularly polarized light [4].

Let the phosphor atoms be initially unpolarized, so that $\boldsymbol{P}_1 = 0$, and the tensor correlation be absent. Thus, the spin density matrix is $\rho_1 = \frac{1}{4} I_4$ (where I_4 is the unit 4×4 matrix). The corresponding density matrix for helium is equal to [3, 4]

$$\rho_2 = \frac{1}{3}\left[1 + \frac{3}{2}\sum_i P_{2i}\hat{S}_{2i} + 3\sum Q_{2ij}\hat{S}_{2ij} \right], \tag{20}$$

where $\hat{S}_{2ij} = \frac{1}{2}\left[\hat{S}_{2i}\hat{S}_{2j} + \hat{S}_{2j}\hat{S}_{2i}\right] - \frac{2}{3}\delta_{ij}$ ($i, j = x, y, z$), and $\hat{S}_{2i}$ is the spin operator $S_2 = 1$. Formalism (5)–(14) yields the following results.

Collision probability (19) is ($N = 3$)

$$\tilde{W} = \frac{1}{6}\left(\left|A_{1/2}\right|^2 + 2\left|A_{3/2}\right|^2\right) = \frac{1}{18}, \tag{21}$$

where

$$A_S \equiv A_S\left(S_1' = 1/2, S_2' = 1\right) = \frac{1}{3}\left[\exp\left(-i\int_{-\infty}^{+\infty} E^S_{1/2,1}\,dt\right)\right] \qquad (S = 1/2,\ 1). \tag{22}$$

Polarization states of atoms after collision (19) are

$$P_{1i}' = \left(\frac{5 - 4\sqrt{10}\cos x}{18}\right)P_{2i}, \quad P_{2i}' = \left(\frac{1 + \sqrt{10}\cos x}{9}\right)P_{2i} \qquad (i = x, y, z), \tag{23}$$

where $x = \int_{-\infty}^{\infty} \Delta_{1/2,3/2}\,dt \equiv \int_{-\infty}^{\infty} (E^{1/2}_{1/2,1} - E^{3/2}_{1/2,1})\,dt = 2\int_{r}^{+\infty} (E^{1/2}_{1/2,1} - E^{3/2}_{1/2,1})\frac{R\,dR}{v\sqrt{R^2 - r^2}}$, v is the velocity of relative motion of the atoms, and the Hartree system of units is used [5].

Other processes of the examined type can be considered analogously.

CONCLUSIONS

Consideration of the problems of slow atomic collisions with changes of spins has demonstrated that the spin polarization has a purely exchange, that is, nonrelativistic character, when the total spin of the system of colliding atoms is conserved. However, it seems likely that deviations from the scheme of the pure LS-bond should be considered for heavy atoms, sending us in search for more adequate approaches to a theoretical description of atomic collisions with changes of spins.

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