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# The role of the Pauli principle in metastability exchange collisions 

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#### Abstract

Résumé. - Dans les expériences de pompage optique, les collisions d'échange de métastabilité peuvent servir à transférer de l'orientation, alignement, etc... entre divers niveaux atomiques. Cet article est consacré à l'étude de telles collisions et de la façon dont elles agissent sur l'opérateur densité décrivant les variables internes des atomes. Le calcul présenté est valable pour des noyaux discernables ou identiques, ce qui rend possible une discussion détaillée des effets d'indiscernabilité des noyaux (champ magnétique fictif, etc...). Deux cas sont étudiés : collisions sans dépolarisation (collisions $\mathrm{He}^{*}-\mathrm{He}$ ), collisions avec dépolarisation partielle ( $\mathrm{Ne}^{*}-\mathrm{Ne}$ par exemple). Les effets d'indiscernabilité nucléaire devraient être observables dans des expériences de pompage optique avec des gaz rares à basse température. Dans un appendice est discuté un autre effet d'indiscernabilité des particules qui peut être observé par des expériences de jets atomiques: au cours de la collision entre deux atomes ${ }^{3} \mathrm{He}$, tous deux dans le niveau fondamental, l'état de spin des atomes diffusés dans une direction particulière peut être changé par un effet d'indiscernabilité des noyaux.


#### Abstract

In optical pumping experiments, metastability exchange collisions are used to transfer orientation, alignment, ... between different atomic levels. This article studies the effect of such collisions on the atom internal variables density operator by a method used in a previous publication for spin exchange collisions. The calculations are valid when the nuclei of the two atoms are distinguishable as well as when they are identical particles, which allows a detailed discussion of nuclear identity effects (apparent magnetic field, etc...). Two cases are successively studied : no depolarization of the electronic angular momentum ( $\mathrm{He}^{*}-\mathrm{He}$ collisions) and partial depolarization ( $\mathrm{Ne}^{*}-\mathrm{Ne}$ collisions for example). The nuclear identity effects should be observable in low temperature optical pumping experiments with noble gases. In an Appendix, another particle identity effect is studied, which can be observed in atomic beam experiments : during the collision of two ${ }^{3} \mathrm{He}$ atoms, both in the ground state, the spin state of the atoms scattered in a particular direction can be changed by nuclear indistinguishability effects.


1. Introduction. - The role of the Pauli principle in spin exchange collisions has been discussed in a previous article [1]. In order to emphasize the effects arising from the particle indistinguishability, all particles were first supposed to be distinguishable, and the Pauli principle was only introduced in a second step. The same method will be used here, but for metastability exchange collisions.

The importance of this type of collision in optical pumping experiments is well known [2]. In helium experiments for example, direct nuclear polarization of the ground state of ${ }^{3} \mathrm{He}$ cannot be achieved by using the optical resonance line for various reasons (this line belongs to the vacuum U.V. part of the spectrum ;

[^0]the hyperfine structure of the $2{ }^{1} \mathrm{P}$ state of ${ }^{3} \mathrm{He}$ is too small to create a nuclear orientation during the radiative lifetime). An indirect optical pumping method can nevertheless be used, as shown by F. D. Colegrove, L. D. Schearer and G. K. Walters [3]. The method consists in using the $\lambda=1.08 \mu$ line of helium ( $2{ }^{3} \mathrm{~S}-2{ }^{3} \mathrm{P}$ transition) to create optically both electronic and nuclear orientations of the $2{ }^{3} \mathrm{~S}_{1}$ metastable state (which has a hyperfine structure of approximately 6 GHz , much larger than its lifetime). The nuclear polarization is then transferred to the ground state of ${ }^{3} \mathrm{He}$ by so called metastability exchange collisions between the $2{ }^{3} \mathrm{~S}_{1}$ and ground state atoms.

The corresponding evolution of the internal variable (I and J) density operator in both states has been studied by R. B. Partridge and G. W. Series [4]. These authors evaluate coherence transfer effects in ${ }^{3} \mathrm{He}$ optical pumping experiments, without including
nuclear identity effects. One of the important physical ideas used is that the nuclear and electronic parts of newly formed metastable atoms are entirely uncorrelated. When the two nuclei can be labelled, it is indeed clear that, after exchange, the metastable atom contains the nucleus which was, before collision, associated with a ground state electronic cloud. On the other hand, when the two nuclei are identical particles, it becomes impossible to tell which one corresponds to a metastable or ground state atom, so that a more careful examination seems to be necessary. One of the aims of the present article is to study precisely to what extent identical particle effects modify the equations obtained for the internal variable evolution. Actually, we shall find that in many practical situations (room temperature experiments, low nuclear polarization), the decorrelation between electronic and nuclear spins, introduced in [4], is the only important effect of metastability exchange. This justifies the use of equations of reference [4] as a starting point for subsequent calculations of the optical pumping process in ${ }^{3} \mathrm{He}$ [5]. Nevertheless, we shall also find that it is possible to design experiments where nuclear identity effects (fictitious magnetic fields) are not negligible, or maybe even dominant under appropriate conditions.

There are in the literature other references concerning the effect of metastability exchange collisions in helium optical pumping. A general paper on metastable excitation transfer by H. J. Kolker and H. H. Michels [6] includes a discussion of nuclear identity effects, but without introducing density operators for the internal atomic variables I and $\mathbf{J}$. These authors show why nuclear identity can rigorously be ignored as far as only populations (longitudinal observables) are of importance in the experiment. This is an interesting result since, for example, it implies that the maximum nuclear orientation obtained by optical pumping does not depend on nuclear identity effects. In section 2.2.2 of this article, we shall discuss this point in detail and show how these effects nevertheless do affect the evolution of the density matrix coherences (which is essential in magnetic resonance experiments). Another related reference is a paper by S. D. Rosner and F. M. Pipkin [7] which gives the uncorrelated part (the part obtained in [4] for distinguishable nuclei) of the density operator and also includes nuclear identity effects. The method we use here is different (we wish to calculate one-atom density operators for example) and some of the results we shall obtain do not coincide with those of reference [7].

Helium is not the only noble gas which can be nuclearly polarized by indirect optical pumping through a metastable state. For example, experiments with ${ }^{21} \mathrm{Ne}[8,9,10]$ can be performed. In such a case, the electronic angular momentum in the ${ }^{3} \mathrm{P}_{2}$ metastable state is no longer a pure spin momentum and some depolarization can occur during the collision. The present article gives a generalization of the
metastability exchange calculations to the general case where the electronic internal variables can be affected by the collision. Since the fact that one of the atoms is metastable does not enter explicitly in the calculation, it can be considered as a general study of the effects of nuclear identity on depolarizing collisions. In many experiments, these collisions occur with the same probability in all directions and the rotational invariance introduces an important simplification : the collision can be described in terms of electronic coefficients $\gamma^{(1)}$ (orientation destruction constant), $\gamma^{(2)}$ (alignment destruction), even in the presence of a nuclear spin which is not affected by the collision $[2,11,12,13]$. We shall see how this formalism must be adapted to take into account energy transfer and nuclear identity effects.

Another particle identity effect, which cannot be observed by optical pumping techniques, is briefly discussed in an Appendix. This effect can be observed in atomic beam experiments where a particular scattering direction is observed, and occurs during the interaction of two ${ }^{3} \mathrm{He}$ atoms, which are both in the ground state. It is related to the subject of this article as far as it is a modification of the atom internal variables arising from the Pauli principle. We shall see that the density operator, describing the internal spin variables of the atoms scattered inside a given solid angle, is affected by particle identity effects. In particular, interference effects occur in the forward direction and change the spin state of the transmitted beam, when the spins of the target and incident beam are not parallel (or antiparallel). This effect is reminiscent of the Faraday effect where the polarization of a light beam is rotated in an anisotropic medium. At low collision energies, we shall see that changes in the spin due to nuclear identity become the most significant.
2. Metastability exchange in helium. - Let us first consider a specific case of metastability exchange collisions between two helium atoms, one in the metastable $2{ }^{3} \mathrm{~S}_{1}$ state, the other in the ground state $1^{1} \mathrm{~S}_{0}$. As mentioned in the introduction, one important feature of these collisions is that practically no depolarization occurs, due to the fact that all angular momenta involved are spins, which are practically not affected in a collision (Wigner rule). In this sense, the situation is exactly similar to spin exchange studied in [1]. The major difference is that the electronic clouds of the two atoms are now different : one atom is in an excited electronic level, with angular momentum $J=S=1$, the other in the ground state with no angular momentum ( $J=L=S=0$ ). The two atoms therefore no longer play a symmetric role in the process under study.

Throughout the present article, the fact that one of the atoms is metastable does not appear explicitly. The calculations are valid for any collision between two atoms in different electronic states, provided
that the collision is elastic and no $\mathbf{J}$ depolarization occurs ( $3{ }^{3} \mathrm{~S}_{1}-1{ }^{1} \mathrm{~S}_{0}$ energy exchange collisions for example). During the collision, the internal variables (orientation, alignment) of the atoms evolve and we wish to study the consequences of the identity of the two atom nuclei on this evolution. We shall see that this identity results in interference effects which are similar to those obtained in the case of spin exchange collisions [1].
2.1 Distinguishable nuclei. - As a first step, let us assume that the nuclei of the two atoms are distinguishable. For example, they correspond to two different isotopes.

### 2.1.1 Notation. - The ket

$$
|1: \mathbf{k}, \mathbf{g} ; 2:-\mathbf{k}, \mathrm{e}\rangle
$$

refers to a state of the atom motion in the centre of
mass frame, one ground state atom having a linear momentum $\hbar \mathbf{k}$ and one excited (metastable) atom having a linear momentum $-\hbar \mathbf{k}$. We assume that the ground state has no internal electronic angular momentum, and denote by $\mathbf{J}$ the electronic momentum of the excited state $(J=1$ in the case of the $2{ }^{3} \mathrm{~S}_{1}$ state). $\mathrm{O} z$ is a fixed reference axis, $M$ is the quantum number associated with the eigenvalue of $J_{z}$. Since the two nuclei may also possess non zero spins, the quantum numbers $m_{I}$ and $m_{I}^{\prime}$ will be used to describe them. A complete description of the two atom system is then given (in the centre of mass reference frame) by the ket :

$$
\left|1: \mathbf{k}, \mathbf{g}, m_{I} ; 2:-\mathbf{k}, \mathrm{e}, m_{I}^{\prime}, M\right\rangle
$$

Another state accessible to the system, with exactly the same energy $\left({ }^{1}\right)$, is :

$$
\left|1: \mathbf{k}, \mathrm{e}, m_{I}, M ; 2:-\mathbf{k}, \mathbf{g}, m_{I}^{\prime}\right\rangle
$$

We now have to write the $S$ matrix elements between such states. Since we assume that no spin modification occurs during the collision, these matrix elements do not depend either on $M$ or on $m_{I}$. We first have direct processes :

$$
\begin{align*}
\left\langle 1: \mathbf{k}_{\mathrm{f}}, \mathrm{~g}, m_{I} ; 2:-\mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}^{\prime}, M\right| S\left|1: \mathbf{k}_{\mathrm{i}}, \mathrm{~g}, m_{I}^{\prime \prime} ; 2:-\mathbf{k}_{\mathrm{i}}, \mathrm{e}, m_{I}^{\prime \prime \prime}, M^{\prime}\right\rangle & = \\
& =\delta_{m_{I} m_{I}^{\prime \prime}} \delta_{m_{I}^{\prime} m_{I}^{\prime \prime}} \delta_{M M^{\prime}} S_{\mathrm{d}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) \tag{1.a}
\end{align*}
$$

(in this equation, the numbers 1 and 2 can be interchanged both in the bra and the ket). Also resonant transfer processes correspond to the matrix elements :

$$
\begin{align*}
\left\langle 1: \mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}, M ; 2:-\mathbf{k}_{\mathrm{f}}, \mathbf{g}, m_{I}^{\prime}\right| S\left|1: \mathbf{k}_{\mathrm{i}}, \mathrm{~g}, m_{I}^{\prime \prime} ; 2:-\mathbf{k}_{\mathrm{i}}, \mathrm{e}, m_{I}^{\prime \prime \prime}, M^{\prime}\right\rangle & = \\
& =\delta_{m_{I} m_{I}^{\prime \prime}} \delta_{m_{I}^{\prime} m_{I}^{\prime \prime \prime}} \delta_{M M^{\prime}} S_{\mathrm{t}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) \tag{1.b}
\end{align*}
$$

2.1.2 Density operator after collision. - The initial density operator of the system is (we use the same notation as in [1]) :

$$
\begin{equation*}
\sigma_{\mathrm{init}}=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathbf{i}}^{\prime}\right)\left|1: \mathbf{k}_{\mathrm{i}}, \mathrm{~g} ; 2:-\mathbf{k}_{\mathrm{i}}, \mathrm{e}\right\rangle\left\langle 1: \mathbf{k}_{\mathrm{i}}^{\prime}, \mathrm{g} ; 2:-\mathbf{k}_{\mathrm{i}}^{\prime}, \mathrm{e}\right| \otimes \rho_{\mathrm{g}}(1) \otimes \rho_{\mathrm{m}}(2, \mathrm{e}) \tag{2}
\end{equation*}
$$

In this equality, $\rho_{\mathrm{g}}(1)$ and $\rho_{\mathrm{m}}(2, \mathrm{e})$ are the internal variable density operators associated respectively with the ground state and excited (metastable) state before collision. After collision, we have to calculate four different density operators : the nucleus 1 spin variable density operator $\bar{\rho}_{\mathrm{g}}(1)$ when this nucleus is associated with a ground state density operator, and the similar operator $\bar{\rho}_{\mathrm{g}}(2)$ for nucleus 2 ; also two density operators $\bar{\rho}_{\mathrm{m}}(1, \mathrm{e})$ and $\bar{\rho}_{\mathrm{m}}(2$, e) describing metastable internal variables with either nucleus 1 or nucleus 2 . We obtain for the two ground state density operators :

$$
\begin{align*}
\left\langle m_{I}\right| \bar{\rho}_{\mathrm{g}}(1)\left|m_{I}^{\prime}\right\rangle & =\int \mathrm{d}^{3} k_{\mathrm{f}} \sum_{m_{I}^{\prime \prime}} \sum_{M^{\prime \prime}} \times \\
& \times\left\langle 1: \mathbf{k}_{\mathrm{f}}, \mathbf{g}, m_{I} ; 2:-\mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}^{\prime \prime}, M^{\prime \prime}\right| S \sigma_{\mathrm{init}} S^{\dagger}\left|1: \mathbf{k}_{\mathrm{f}}, \mathrm{~g}, m_{I}^{\prime} ; 2:-\mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}^{\prime \prime}, M^{\prime \prime}\right\rangle \tag{3.a}
\end{align*}
$$

and :

$$
\begin{align*}
\left\langle m_{I}\right| \bar{\rho}_{\mathrm{g}}(2)\left|m_{I}^{\prime}\right\rangle & =\int \mathrm{d}^{3} k_{\mathrm{f}} \sum_{m_{I}^{\prime \prime}} \sum_{M^{\prime \prime}} \times \\
\times & \left.<1: \mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}^{\prime \prime}, M^{\prime \prime} ; 2:-\mathbf{k}_{\mathrm{f}}, \mathrm{~g}, m_{I}\left|S \sigma_{\mathrm{init}} S^{\dagger}\right| 1: \mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}^{\prime \prime}, M^{\prime \prime} ; 2:-\mathbf{k}_{\mathrm{f}}, \mathbf{g}, m_{I}^{\prime}\right\rangle \tag{3.b}
\end{align*}
$$

[^1]For the metastable state density operators, the result is :

$$
\begin{align*}
\left\langle m_{I} M\right| \bar{\rho}_{\mathrm{m}}(1, \mathrm{e})\left|m_{I}^{\prime} M^{\prime}\right\rangle & =\int \mathrm{d}^{3} k_{\mathrm{f}} \sum_{m_{I}^{\prime \prime}} \times \\
\times & \left\langle 1: \mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}, M ; 2:-\mathbf{k}_{\mathrm{f}}, m_{I}^{\prime \prime}\right| S \rho_{\mathrm{init}} S^{\dagger}\left|1: \mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}^{\prime}, M^{\prime} ; 2:-\mathbf{k}_{\mathrm{f}}, m_{I}^{\prime \prime}\right\rangle \tag{4}
\end{align*}
$$

For $\bar{\rho}_{\mathrm{m}}(2, \mathrm{e})$, an analogous expression is obtained by simply interchanging the numbers 1 and 2 in (4).
Using (1), (2), (3) and (4), one then obtains :

$$
\begin{align*}
\left\langle m_{I}\right| \rho_{\mathrm{g}}(1)\left|m_{I}^{\prime}\right\rangle=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathbf{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathbf{i}}^{\prime}\right) & \int \mathrm{d}^{3} k_{\mathrm{f}} S_{\mathrm{d}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S_{\mathrm{d}}^{*}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathbf{i}}^{\prime}\right) \times \\
& \times \sum_{m^{\prime \prime}} \sum_{M^{\prime \prime}}\left\langle m_{I}\right| \rho_{\mathrm{g}}(1)\left|m_{I}^{\prime}\right\rangle\left\langle m_{I}^{\prime \prime} M^{\prime \prime}\right| \rho_{\mathrm{m}}(2, \mathrm{e})\left|m_{I}^{\prime \prime} M^{\prime \prime}\right\rangle \tag{5}
\end{align*}
$$

that is :

$$
\begin{equation*}
\bar{\rho}_{\mathrm{g}}(1)=A_{\mathrm{d}} \rho_{\mathrm{g}}(1) \tag{6}
\end{equation*}
$$

with :

$$
\begin{equation*}
A_{\mathrm{d}}=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathbf{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \int \mathrm{d}^{3} k_{\mathrm{f}} S_{\mathrm{d}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S_{\mathrm{d}}^{*}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right) . \tag{7}
\end{equation*}
$$

Similarly, if we set :

$$
\begin{equation*}
A_{\mathrm{t}}=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathbf{i}}^{\prime}\right) \int \mathrm{d}^{3} k_{\mathrm{f}} S_{\mathrm{t}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S_{\mathrm{t}}^{*}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathbf{i}}^{\prime}\right) \tag{8}
\end{equation*}
$$

we obtain :

$$
\begin{equation*}
\left\langle m_{I}\right| \bar{\rho}_{\mathrm{g}}(2)\left|m_{I}^{\prime}\right\rangle=A_{\mathrm{t}} \sum_{m_{I}^{\prime \prime}} \sum_{M^{\prime \prime}}\left\langle m_{I} M^{\prime \prime}\right| \rho_{\mathrm{m}}(2, \mathrm{e})\left|m_{I}^{\prime} M^{\prime \prime}\right\rangle\left\langle m_{I}^{\prime \prime}\right| \rho_{\mathrm{g}}(1)\left|m_{I}^{\prime \prime}\right\rangle \tag{9}
\end{equation*}
$$

or :

$$
\begin{equation*}
\bar{\rho}_{\mathrm{g}}(2)=A_{\mathrm{t}} \operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}(2, \mathrm{e})\right\} \tag{10}
\end{equation*}
$$

[ $\operatorname{Tr}_{J}$ denotes the trace operation over the electronic angular momentum variables]. As for the two excited state density operators, they can be obtained by analogous calculations. One finds :

$$
\begin{align*}
\left\langle m_{I} M\right| \bar{\rho}_{\mathrm{m}}(1, \mathrm{e}) \mid m_{I}^{\prime} M^{\prime} & \rangle=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \times \\
\times & \int \mathrm{d}^{3} k_{\mathrm{f}} S_{\mathrm{t}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S_{\mathrm{t}}^{*}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right) \sum_{m_{I}^{\prime \prime}}\left\langle m_{I}\right| \rho_{\mathrm{g}}(1)\left|m_{I}^{\prime}\right\rangle\left\langle m_{I}^{\prime \prime} M\right| \rho_{\mathrm{m}}(2, \mathrm{e})\left|m_{I}^{\prime \prime} M^{\prime}\right\rangle \tag{11}
\end{align*}
$$

or :

$$
\begin{equation*}
\bar{\rho}_{\mathrm{m}}(1, \mathrm{e})=A_{\mathrm{t}} \rho_{\mathrm{g}}(1) \otimes \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}(2, \mathrm{e})\right\} \tag{12}
\end{equation*}
$$

Finally, $\bar{\rho}_{\mathrm{m}}(2, \mathrm{e})$ is given by :

$$
\begin{equation*}
\bar{\rho}_{\mathrm{m}}(2, \mathrm{e})=A_{\mathrm{d}} \rho_{\mathrm{m}}(2, \mathrm{e}) \tag{13}
\end{equation*}
$$

Before discussing the physical interpretation of these results, it can be remarked that :

$$
\begin{equation*}
A_{\mathrm{t}}+A_{\mathrm{d}}=1 \tag{14}
\end{equation*}
$$

so that $A_{\mathrm{d}}$ will be replaced by $1-A_{\mathrm{t}}$ in all subsequent calculations. The proof of (14) is quite analogous to the proof of (12) in [1] and exploits the unitary character of the operator $S$. Relation (14) insures that :

$$
\begin{equation*}
\operatorname{Tr}\left\{\bar{\rho}_{\mathrm{g}}(1)\right\}+\operatorname{Tr}\left\{\bar{\rho}_{\mathrm{m}}(1, \mathrm{e})\right\}=1 \tag{15}
\end{equation*}
$$

2.1.3 Physical interpretation. - The interpretation of (6) is straightforward : since $I$ is not affected at all by the collision, the density operator of nucleus 1 after collision is merely proportional to its value before collision. The proportionality coefficient is nothing but the probability that no electronic energy transfer will occur during the collision. Equation (10) shows that, if such an energy transfer actually occurs, the density matrix of atom 2 in the ground electronic state is the partial trace over electron spin variables of the initial excited state density matrix. Again, this is easily understood in terms of complete inertia of $\mathbf{I}$ during the collision.

Equations (12) and (13) can be commented on in the same fashion. The latter shows that direct processes do not alter the excited state density operator. The former indicates that, just after a transfer collision, the
internal density operator of the excited state is nothing but the tensor product of the initial ground state (nuclear) density operator by the trace over nuclear spin variables of the initial excited state density operator (this trace is an electronic spin operator).

Let us now assume that the nuclear spins of atoms 1 and 2 have the same value, and that nothing in the experiment considered allows to differentiate species 1 from species 2 . We then define the total ground state density operator by :

$$
\rho_{\mathrm{g}}=\rho_{\mathrm{g}}(1)+\rho_{\mathrm{g}}(2)
$$

and the excited state density operator by :

$$
\rho_{\mathrm{m}}=\rho_{\mathrm{m}}(1, \mathrm{e})+\rho_{\mathrm{m}}(2, \mathrm{e})
$$

One then easily sees that each metastability exchange collisions changes :

$$
\rho_{\mathrm{g}} \text { into }\left(1-A_{\mathrm{t}}\right) \rho_{\mathrm{g}}+A_{\mathrm{t}} \operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}
$$

and :

$$
\rho_{\mathrm{m}} \quad \text { into } \quad\left(1-A_{\mathrm{t}}\right) \rho_{\mathrm{m}}+A_{\mathrm{t}} \rho_{\mathrm{g}} \otimes \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}
$$

If we consider an ensemble of ground state and metastable state atoms, with number densities $n_{\mathrm{g}}$ and $n_{\mathrm{m}}$ respectively, the internal variable density operator $\rho_{\mathrm{g}}$ and $\rho_{\mathrm{m}}$ evolution due to collisions is :

$$
\begin{equation*}
\left.\frac{\mathrm{d}}{\mathrm{~d} t} \rho_{\mathrm{g}}\right|_{\text {coll }}=\frac{1}{T_{\text {coll }}}\left[-\rho_{\mathrm{g}}+\operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}\right] \tag{16.a}
\end{equation*}
$$

and :

$$
\begin{equation*}
\left.\frac{\mathrm{d}}{\mathrm{~d} t} \rho_{\mathrm{m}}\right|_{\text {coll }}=\frac{1}{\tau_{\text {coll }}}\left[-\rho_{\mathrm{m}}+\rho_{\mathrm{g}} \otimes \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}\right] \tag{16.b}
\end{equation*}
$$

where:

$$
\begin{equation*}
\frac{T_{\text {coll }}}{\tau_{\text {coll }}}=\frac{n_{\mathrm{g}}}{n_{\mathrm{m}}} \tag{17}
\end{equation*}
$$

These equations are exactly equivalent to equations (5.a) and (5.b) of Partridge and Series [4].
2.2 Indistinguishable nuclei. - We now consider collisions between atoms of the same isotope having indistinguishable nuclei. If $P_{\mathrm{n}}$ is the exchange operator between these nuclei, the initial density operator of the 2 atoms is given by :

$$
\frac{1}{2}\left[1-P_{\mathrm{n}}\right] \sigma_{\text {init }}\left[1-P_{\mathrm{n}}\right]
$$

We assume here that the nuclei are fermions but, to treat the case when they are bosons, it is sufficient to replace $1-P_{\mathrm{n}}$ by $1+P_{\mathrm{n}}$.
2.2.1 Internal density operator after collision. Let us calculate for example the excited state internal variable density operator $\bar{\rho}_{\mathrm{m}}$ after collision. This calculation is very similar to the one of section 2.2 of reference [1]. The analogue of equation (19) of this reference is now :

$$
\begin{align*}
& \left\langle m_{I}, M\right| \bar{\rho}_{\mathrm{m}}\left|m_{I}^{\prime}, M^{\prime}\right\rangle=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \int \mathrm{d}^{3} k_{\mathrm{f}} \sum_{m_{I}^{\prime \prime}} \times \\
& \quad \times\left\langle 1:-\mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}, M ; 2: \mathbf{k}_{\mathrm{f}}, \mathrm{~g}, m_{I}^{\prime \prime}\right|\left[1-P_{\mathrm{n}}\right] S \sigma_{\mathrm{init}} S^{\dagger}\left[1-P_{\mathrm{n}}\right]\left|1:-\mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}^{\prime}, M^{\prime} ; 2: \mathbf{k}_{\mathrm{f}}, \mathrm{~g}, m_{I}^{\prime \prime}\right\rangle \tag{18}
\end{align*}
$$

where $\sigma_{\text {init }}$ is given by (2). As in the spin exchange calculation, the two terms which contain either no $P_{n}$ or two such operators give the result already obtained for distinguishable nuclei :

$$
A_{\mathrm{t}} \rho_{\mathrm{g}} \otimes \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}+\left(1-A_{\mathrm{t}}\right) \rho_{\mathrm{m}}
$$

The two terms which contain one exchange operator $P_{\mathrm{n}}$ are new, and they are equal to :

$$
-\left\{\bar{C}_{I} \rho_{\mathrm{m}} \times\left(\rho_{\mathrm{g}} \otimes \mathbb{1}_{J}\right)+\bar{C}_{I}^{*}\left(\rho_{\mathrm{g}} \otimes \mathbb{1}_{J}\right) \times \rho_{\mathrm{m}}\right\}
$$

where :

$$
\begin{align*}
\bar{C}_{I}=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) & \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \times \\
& \times \int \mathrm{d}^{3} k_{\mathrm{f}} S_{\mathrm{d}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S_{\mathrm{t}}^{*}\left(-\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right) \tag{19}
\end{align*}
$$

and ${\tau_{J}}_{J}$ is the identity operator in the electronic angular
momentum state space. $\bar{C}_{I}$ is a pure imaginary coefficient:

$$
\begin{equation*}
\bar{C}_{I}=i A_{\mathrm{exch}}^{I} \tag{20}
\end{equation*}
$$

where $A_{\text {exch }}^{I}$ is real. The proof is very similar to the proof of (23) in reference [1] and one can show that:

$$
\begin{align*}
& \bar{C}_{I}+\bar{C}_{I}^{*}=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\underset{\mathbf{k}_{\mathrm{i}}}{ }\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \times \\
& \quad \times\left\langle 1:-\mathbf{k}_{\mathrm{i}}^{\prime}, \mathrm{e} ; 2: \mathbf{k}_{\mathrm{i}}^{\prime}, \mathrm{g}\right| S^{\dagger} S\left|1: \mathbf{k}_{\mathrm{i}}, \mathrm{~g} ; 2:-\mathbf{k}_{\mathrm{i}}, \mathrm{e}\right\rangle \tag{21}
\end{align*}
$$

which vanishes because the internal states e and $g$ are orthogonal.

Then, we obtain :

$$
\begin{align*}
& \bar{\rho}_{\mathrm{m}}=\left(1-A_{\mathrm{t}}\right) \rho_{\mathrm{m}}+A_{\mathrm{t}} \rho_{\mathrm{g}} \otimes \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}- \\
& -i A_{\mathrm{exch}}^{I}\left[\rho_{\mathrm{m}}, \rho_{\mathrm{g}} \otimes \mathcal{1}_{\mathrm{J}}\right] . \tag{22}
\end{align*}
$$

As for the density operator of the ground state after collision, $\bar{\rho}_{\mathrm{g}}$, it can be obtained exactly by the same method. A simple calculation shows that :

$$
\begin{align*}
\bar{\rho}_{\mathrm{g}}=\left(1-A_{\mathrm{t}}\right) \rho_{\mathrm{g}}+ & A_{\mathrm{t}} \\
& \operatorname{rr}_{J}\left\{\rho_{\mathrm{m}}\right\}-  \tag{23}\\
& -i A_{\mathrm{exch}}^{I}\left[\rho_{\mathrm{g}}, \operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}\right]
\end{align*}
$$

When the nuclei of the two colliding atoms are identical, equation (16.a) and (16.b) must therefore be replaced by :

$$
\begin{align*}
& \left.\frac{\mathrm{d}}{\mathrm{~d} t} \rho_{\mathrm{g}}\right|_{\text {coll }}=\frac{1}{T_{\text {coll }}} \times \\
& \quad \times\left\{-\rho_{\mathrm{g}}+\operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}+i \kappa_{I}\left[\operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}, \rho_{\mathrm{g}}\right]\right\} \tag{24}
\end{align*}
$$

and :

$$
\begin{align*}
& \left.\frac{\mathrm{d}}{\mathrm{~d} t} \rho_{\mathrm{m}}\right|_{\text {coll }}=\frac{1}{\tau_{\mathrm{coll}}} \times \\
& \quad \times\left\{-\rho_{\mathrm{m}}+\rho_{\mathrm{g}} \otimes \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}+i \kappa_{I}\left[\rho_{\mathrm{g}} \otimes \mathbb{1}_{J}, \rho_{\mathrm{m}}\right]\right\} \tag{25}
\end{align*}
$$

with :

$$
\begin{equation*}
\kappa_{I}=\frac{A_{\mathrm{exch}}^{I}}{A_{\mathrm{t}}} \tag{26}
\end{equation*}
$$

( $\kappa_{I}$ differs from the coefficient $\kappa$ of reference [7]; see Appendix).
2.2.2 Discussion. - The terms in $\kappa_{I}$ appearing in (24) and (25) are due to the Pauli antisymmetrization principle. Both terms are commutators, and therefore can be accounted for by the introduction of effective hamiltonians inside the ground and excited states. These hamiltonians act only on the nuclear spin variables, which is not surprising since they result from nuclear identity effects.

If we introduce the two partial traces :

$$
\begin{align*}
\rho_{\mathrm{m}}^{I} & =\operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}  \tag{27.a}\\
\rho_{\mathrm{m}}^{J} & =\operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\} \tag{27.b}
\end{align*}
$$

it is possible to check on equations (22) and (23) that the metastability exchange process changes the correlations between I and $\mathbf{J}$ variables, but not their properties as isolated systems (the nuclear spin system including both nuclei). The equality :

$$
\begin{equation*}
\bar{\rho}_{\mathrm{m}}^{J}=\rho_{\mathrm{m}}^{J} \tag{28}
\end{equation*}
$$

is practically obvious on (22) [the fictitious hamiltonian does not act on the $\mathbf{J}$ variables]. In addition, since :

$$
\operatorname{Tr}_{J}\left\{\left[\rho_{\mathrm{m}},\left(\rho_{\mathrm{g}} \otimes \mathbb{U}_{J}\right)\right]\right\}=\left[\rho_{\mathrm{m}}^{I}, \rho_{\mathrm{g}}\right]
$$

we see that the collision changes $\rho^{I}+\rho_{\mathrm{g}}$ into :

$$
\begin{gather*}
\bar{\rho}_{\mathrm{m}}^{I}+\bar{\rho}_{\mathrm{g}}=\left(1-A_{\mathrm{t}}\right) \rho_{\mathrm{m}}^{I}+A_{\mathrm{t}} \rho_{\mathrm{g}}-i A_{\mathrm{exch}}^{I}\left[\rho_{\mathrm{m}}^{I}, \rho_{\mathrm{g}}\right]+ \\
+\left(1-A_{\mathrm{t}}\right) \rho_{\mathrm{g}}+A_{\mathrm{t}} \rho_{\mathrm{m}}^{I}-i A_{\mathrm{exch}}^{I}\left[\rho_{\mathrm{g}}, \rho_{\mathrm{m}}^{I}\right]= \\
=\rho_{\mathrm{g}}+\rho_{\mathrm{m}}^{I} \tag{29}
\end{gather*}
$$

As expected, the total nucleus density operator is
therefore unaffected, owing to the compensation of the effects of the two effective nuclear hamiltonians.

One can also see that, when both $\rho_{\mathrm{m}}$ and $\rho_{\mathrm{g}}$ are close to multiples of unity matrices (that is when orientation, alignment, etc... are weak), the Pauli principle terms can be neglected. This is because commutators are of second order with respect to orientation, alignment, etc... A similar result was obtained in the study of spin exchange collisions [1]. In most optical pumping experiments, where the pumping light is obtained from a discharge lamp, only relatively weak nuclear polarizations are obtained ( $\leqslant 20 \%$ in the case of ${ }^{3} \mathrm{He}$ for example), so that the apparent magnetic fields arising from metastability exchange can be neglected in practice. They should nevertheless be observable in experiments with a high nuclear polarization (laser optical pumping) and at low temperatures (at vanishing collision energies, the coefficient $\kappa_{I} \propto A_{\text {exch }}^{I}$ becomes much larger than $A_{\mathrm{t}}$; see Appendix).
A discussion in terms of interference between direct and transfer processes can be given as in the case of spin exchange. Here, only two diagrams can lead to physically indistinguishable final states (cf. Fig. 1).


Fig. 1. - Two different scattering processes for labelled nuclei $n_{1}$ and $\mathrm{n}_{2}$ are shown schematically in figures (a) and (b). Before and after collision, one atom is in the ground state (g), the other in the excited state (e). When the nuclei are distinguishable, these two diagrams connect the same initial state to two orthogonal, physically different, final states. For identical nuclei, the final states become physically indistinguishable. Interference effects then occur, giving rise to apparent magnetic fields acting on the nuclear spins of the atoms.

If they are denoted by $a$ and $b$ respectively, $|a|^{2}$ corresponds to the first term in the right hand side of (24) and (25), $|b|^{2}$ to the second (metastability exchange) term, the interference term $a b^{*}+b^{*} a$ to the commutators (Pauli principle terms).

Let us now discuss in more detail the experimental conditions under which the nuclear identity effects are observable. We have already mentioned, in the
introduction, the work of H. J. Kolker and H. H. Michels [6]. These authors discuss nuclear symmetry effects in general and state that these effects cancel out in an optical pumping experiment for studying metastability exchange, since only those collisions resulting in a net change in the total population of a magnetic substate are detected. Physically, when two nuclei are in different spin states, they can in principle always be distinguished by their spin (the collision does not change spin directions), so that it is possible to consider them as non-identical particles. Equations (24) and (25) allow us to perform a more detailed discussion of this idea. We shall see that, if phenomena like optical pumping orientation buildup (longitudinal orientations) are indeed insensitive to nuclear symmetry effects, others may depend on these effects (for example the precession of transverse orientations, not considered in [6]). We shall first discuss the ${ }^{3} \mathrm{He}$ ground state evolution, and then the metastable state.

## (i) Ground state evolution.

In the case of ${ }^{3} \mathrm{He}$, the nuclear spin is $I=1 / 2$ and the $2 \times 2$ density matrices $\rho_{\mathrm{g}}$ and $\operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}$ are entirely defined by the nuclear orientations $\langle\mathbf{I}\rangle_{\mathrm{g}}$ and $\langle\mathbf{I}\rangle_{\mathrm{m}}$ inside the ground and metastable levels. Equation (24) shows that the orientation $\langle I\rangle_{m}$ acts on $\langle\mathbf{I}\rangle_{\mathrm{g}}$ like an apparent magnetic field proportional to $\kappa_{I}\langle\mathbf{I}\rangle_{\mathrm{m}}$. Thus, if $\langle\mathbf{I}\rangle_{\mathrm{g}}$ and $\langle\mathbf{I}\rangle_{\mathrm{m}}$ are parallel (or antiparallel), the Pauli principle term does not affect the ground state evolution at all. On the other hand, as shown for example in [5], the effectiveness of metastability exchange collisions constantly tends to equalize $\langle\mathbf{I}\rangle_{\mathrm{m}}$ and $\langle\mathbf{I}\rangle_{\mathrm{g}}$, at least in room temperature experiments where the metastability exchange cross section is relatively large : with a helium pressure of the order of 1 torr, $\langle\mathbf{I}\rangle_{\mathrm{m}}$ follows $\langle\mathbf{I}\rangle_{\mathrm{g}}$ in a time $\tau_{\text {coll }} \simeq 10^{-7} \mathrm{~s}$. Other causes of evolution in the metastable state are the pumping process and wall relaxation, with corresponding time constants $\tau_{\mathrm{p}}$ and $\tau_{\mathrm{r}}$ usually of the order of $10^{-3}$ or $10^{-4} \mathrm{~s}$ (we suppose that the pumping source is a discharge lamp, not a laser). Therefore, if there are no other causes for evolution of the metastable orientations (the effect of the evolution due to magnetic fields is discussed below), $\langle\mathbf{I}\rangle_{\mathrm{m}}$ and $\langle\mathbf{I}\rangle_{\mathrm{g}}$ differ by only a few $10^{-3}$ in relative value. In such a case, the Pauli principle term in (24) is obviously completely negligible and the effect of nuclear identity can be ignored, as stated in [6].

Other situations can nevertheless be found where the two nuclear orientations are not necessarily equal. A first example is given by low temperature experiments : the He metastability exchange cross section drops very rapidly when the collision energy decreases [14, 15] and, at a few degrees Kelvin, $\langle\mathbf{I}\rangle_{\mathrm{m}}$ is no longer very effectively coupled to $\langle\mathbf{I}\rangle_{g}$. With a strong optical pumping source, it should be possible to maintain non parallel values for $\langle\mathbf{I}\rangle_{\mathrm{m}}$ and $\langle\mathbf{I}\rangle_{\mathrm{g}}$. Under these conditions, each orientation defines a
different quantization axis and it is no longer possible to exclude nuclear identity effects by the reasoning mentioned above (which was made in terms of populations only). Physically, two nuclei with non-antiparallel spins cannot be identified with certainty by any spin measurement in quantum mechanics, and nuclear identity effects may then occur.

Another way of obtaining non-parallel directions for $\langle\mathbf{I}\rangle_{\mathrm{g}}$ and $\langle\mathbf{I}\rangle_{\mathrm{m}}$ is to perform a magnetic resonance experiment in the ground state. When $\omega_{\mathrm{m}} \tau_{\text {coll }} \gg 1$ ( $\omega_{\mathrm{m}}$ : Larmor precession frequency of the electron spin in the magnetic field $\mathbf{B}_{0}$ ), the coupling between the transverse components of $\langle\mathbf{I}\rangle_{\mathrm{g}}$ and the metastable variables is completely non-secular, so that $\langle\mathbf{I}\rangle_{\mathrm{m}}$ remains practically parallel to $\mathbf{B}_{0}$ whatever the direction of $\langle\mathbf{I}\rangle_{\mathrm{g}}$. A shift and a distortion of the ground state magnetic resonance curve then results from the term in $\kappa_{I}$. A more detailed discussion of a similar phenomenon will be given below for the resonance curves in the two hyperfine sublevels of the metastable state (where the hyperfine structure allows to perform more varied types of magnetic resonance experiments).

The shift discussed here should not be confused with another shift, proportional to $A_{\mathrm{t}}$ (instead of $A_{\text {exch }}^{I}$ ) which arises from coupling of coherences of the ground and metastable states when $\omega_{\mathrm{m}} \tau \simeq 1[16,17]$.
(ii) Metastable state evolution.

Equation (25) shows that the ground state nuclear orientation $\langle\mathbf{I}\rangle_{\mathrm{g}}$ acts on the metastable level like an apparent magnetic field proportional to $\kappa_{I}\langle\mathbf{I}\rangle_{g}$, only coupled with the metastable nuclear variables (no direct coupling with $\mathbf{J}$ ). The fact that two hyperfine sublevels $F=1 / 2$ and $3 / 2$ occur in the metastable states results in a little more complexity than for the discussion of the ground state evolution.

The conceptually simplest case occurs when :

$$
\rho_{\mathrm{m}} \propto \rho_{\mathrm{m}}^{I} \otimes \rho_{\mathrm{m}}^{J}
$$

The $\mathbf{I}$ and $\mathbf{J}$ variables are then completely uncorrelated. According to (25), no correlation is created by metastability exchange collisions themselves (of course, the strong hyperfine coupling inside the $2{ }^{3} \mathrm{~S}_{1}$ level tends to correlate $\mathbf{I}$ and $\mathbf{J}$, but for the sake of simplicity, we first ignore this fact). The nuclear identity term is then proportional to :

$$
\rho_{\mathrm{m}}^{J} \otimes\left[\rho_{\mathrm{g}}, \rho_{\mathrm{m}}^{I}\right]
$$

which is zero whenever $\rho_{\mathrm{g}}$ and $\rho_{\mathrm{m}}^{I}$ commute with each other (that is when $\langle\mathbf{I}\rangle_{\mathrm{g}}$ and $\langle\mathbf{I}\rangle_{\mathrm{m}}$ are parallel). The situation is the same as for the ground state evolution : the Pauli principle terms subsist only when $\langle\mathbf{I}\rangle_{\mathrm{g}}$ and $\langle\mathbf{I}\rangle_{\mathrm{m}}$ define different quantization axes. In other words, they subsist if $\rho_{\mathrm{m}}$ has non-zero coherences when $\rho_{\mathrm{g}}$ is diagonal.
In the general case where $\mathbf{I}$ and $\mathbf{J}$ are correlated, a convenient basis is given by the coupled $\left|F, m_{F}\right\rangle$
states. In this case also, we shall see that nuclear identity terms are related to the existence of coherences. The fictitious hamiltonian in $\kappa_{I} I$ has two kinds of matrix elements : elements coupling states belonging to the same $F=3 / 2$ or $F=1 / 2$ multiplicity (including diagonal elements), and elements coupling the two hyperfine multiplicities. Since the fictitious hamiltonian is much smaller than the hyperfine coupling, we shall neglect the second kind of matrix elements which have only a non-secular effect (coupling of hyperfine coherences with populations or Zeeman coherences; we assume here that the static magnetic field is not strong enough to decouple the $2{ }^{3} \mathrm{~S}_{1}$ hyperfine structure). The Wigner-Eckart theorem can then be used to conclude that the apparent nuclear field is proportional to $\mathbf{F}$ within each $F$ multiplicity :

$$
\left.\begin{array}{l}
P_{3 / 2} I P_{3 / 2}=\frac{1}{3} P_{3 / 2} \mathrm{~F}  \tag{30}\\
P_{1 / 2} \mathrm{I} P_{1 / 2}=-\frac{1}{3} P_{1 / 2} \mathbf{F}
\end{array}\right\}
$$

( $P_{3 / 2}$ and $P_{1 / 2}$ are the projectors onto the $F=3 / 2$ and $1 / 2$ multiplicities). The effect of the effective hamiltonian is to introduce two opposite precessions around $\langle\mathbf{I}\rangle_{\mathrm{g}}$ inside the two hyperfine sublevels ( ${ }^{2}$ ). When the static magnetic field $\mathbf{B}_{0}$ is not zero, these precessions are additional to the Zeeman precessions in these sublevels. Since the Landé factors are $g_{3 / 2}=4 / 3$ and $g_{1 / 2}=8 / 3$, it is equivalent to say that two apparent magnetic fields $\mathbf{B}_{3 / 2}^{I}$ and $\mathbf{B}_{1 / 2}^{I}$ are added to $\mathbf{B}_{0}$ (see Fig. 2), with :

$$
\begin{equation*}
\mathbf{B}_{3 / 2}^{I}=-2 \mathbf{B}_{1 / 2}^{I} \propto \kappa_{I}\langle\mathbf{I}\rangle_{\mathrm{g}} . \tag{31}
\end{equation*}
$$

As long as $\left|\mathbf{B}_{1 / 2,3 / 2}^{I}\right| \ll\left|\mathbf{B}_{0}\right|$, the components of these fields normal to $\mathbf{B}_{0}$ can be neglected.

Let us assume that $\langle\mathbf{I}\rangle_{\mathrm{g}}$ is parallel to $\mathbf{B}_{0}$ which defines the $\mathrm{O} z$ axis. When the metastable density matrix $\rho_{\mathrm{m}}$ has no coherences between different Zeeman or hyperfine sublevels, it is clear that $\mathbf{B}_{1 / 2}^{I}$ and $\mathbf{B}_{3 / 2}^{I}$ have no effect : they just slightly change the energy level position, which does not affect the evolution of the various populations. Such a case occurs, for example, during the transient optical buildup of the longitudinal polarization in the coupled ground and metastable states. We see that nuclear identity effects are then absent (if one excepts the non-secular creation of hyperfine $\Delta m=0$ coherences from populations due to off-diagonal matrix elements of the effective hamiltonian). On the other hand, if there are Zeeman or hyperfine coherences in $\rho_{\mathrm{m}}$, the apparent fields $\mathbf{B}_{3 / 2}^{I}$ and $\mathbf{B}_{1 / 2}^{I}$ change the corresponding evolution frequencies (figure 2 can be used to see the modifications of the various Bohr frequencies). The

[^2]

Fig. 2. - Energies of the Zeeman and hyperfine sublevels of an ${ }^{3} \mathrm{He}$ atom in the metastable state, as a function of the static magnetic field $B_{0}$. The zero-field hyperfine structure is about 6.7 GHz and no hyperfine decoupling is supposed to occur. When the ground state of the ${ }^{3} \mathrm{He}$ atoms is nuclearly polarized, metastability exchange collisions create fictitious magnetic fields $B_{1 / 2}^{I}$ and $B_{3 / 2}^{I}$, which have opposite signs for the $F=1 / 2$ and $F=3 / 2$ sublevels [we assume in this figure that $\langle\mathbf{I}\rangle_{\mathrm{g}}$ and $\mathbf{B}_{0}$ are parallel, and that $\kappa\left\langle I_{z}\right\rangle_{\mathrm{g}}$ is positive]. Figure 3 shows the resulting shift and distortion of the magnetic resonance curves.
fictitious nuclear field may then have an important effect on the metastable state evolution.

If, for example, a magnetic resonance experiment in the $F=1 / 2$ sublevel is performed, the apparent field will clearly result in a change of the resonance line position and shape. As discussed in reference [5], the metastability exchange collisions produce an effective coupling between the longitudinal orientations $\left\langle\mathbf{I}_{z}\right\rangle_{g},\left\langle\mathbf{F}_{z}\right\rangle_{1 / 2}$ and $\left\langle\mathbf{F}_{z}\right\rangle_{3 / 2}$, but the coupling between the transverse orientations can be neglected (the only level with non-negligible transverse orientation is the $F=1 / 2$ sublevel). The resonance can be monitored by measuring any of the longitudinal orientations, $\left\langle I_{z}\right\rangle_{\mathrm{g}}$ for example, and a convenient way to do this is to detect the polarization of optical lines emitted by the discharge in helium [18]. If $\langle\mathbf{I}\rangle_{\mathrm{g}}$ were constant, $\mathbf{B}_{1 / 2}^{I}$ would also be constant and the fictitious field would simply shift the magnetic resonance position for the $F=1 / 2$ sublevel. This is actually a good approximation if the radiofrequency field is weak enough to produce small relative variations of the longitudinal orientations. A possible experiment would then consist in doing magnetic resonance with a weak radiofrequency field, and comparing the resonance positions for different values and signs of the longitudinal orientations (which can be produced by using different pump intensities or reversing the pump polarization). When the radiofrequency is stronger and induces large relative variations of $\left\langle I_{z}\right\rangle$, the shift of the resonance curve depends on the value of $\left\langle I_{z}\right\rangle$. The geometrical construction of the new, non-Lorentzian, curve is shown in figure 3.

Magnetic resonance experiments in the $F=3 / 2$


Fig. 3. - Geometrical construction of the magnetic resonance curve inside the $F=1 / 2$ hyperfine sublevel. $\left\langle I_{z}\right\rangle_{\mathrm{g}}$ is the longitudinal ground state orientation, $\mathbf{B}_{0}$ the static field (parallel to Oz ), $B_{1 / 2}^{I}$ the apparent field acting in the $F=1 / 2$ sublevel and arising from nuclear exchange (an analogous construction is possible for the $F=3 / 2$ sublevel, but the apparent field has to be multiplied by -2 ). Since all levels are strongly coupled by metastability exchange, the resonant variations of $\left\langle I_{z}\right\rangle_{\mathrm{g}},\left\langle F_{z}\right\rangle_{3 / 2}$ and $\left\langle F_{z}\right\rangle_{1 / 2}$ are simply proportional. The apparent magnetic field $B_{1 / 2}^{I}$ is proportional to $\left\langle I_{z}\right\rangle_{\mathrm{g}}$ so that the resonance curve obtained (full line) is shifted and distorted, as compared to the curve which would be obtained in the absence of nuclear identity effects (broken line).
hyperfine sublevel can also be performed. This does not necessary require the presence of an orientation, since the creation of an alignment is then possible. The resonance shift and distortion can then be suppressed by using a linear pump polarization which creates no ground state orientation.

Another type of experiment would be to detect the resonance of the hyperfine coherences, with an oscillating magnetic field at about 6.7 GHz , as in the experiment performed by S. D. Rosner and F. M. Pip-
kin [19]. The frequency shifts of the various coherences are directly visible in figure 2 .

We see that there are various possibilities to detect nuclear identity effects by magnetic resonance in the metastable states (actually, even when $\langle\mathbf{I}\rangle_{\mathrm{m}}=\langle\mathbf{I}\rangle_{\mathrm{g}}$, some effects can be expected, in opposition to the ground state resonance). To our knowledge, the predicted shifts and distortions of the curves have not yet been observed.

## Remarks :

(i) The preceding calculation can be applied to metastability exchange collisions for $2{ }^{1} \mathrm{~S}_{0}$ metastable states. The situation is then even simpler since no electronic spin is then involved. Equations (22) and (23) become, in this case :

$$
\begin{align*}
& \bar{\rho}_{\mathrm{m}}=\left(1-A_{\mathrm{t}}\right) \rho_{\mathrm{m}}+A_{\mathrm{t}} \rho_{\mathrm{g}}-i A_{\mathrm{exch}}^{I}\left[\rho_{\mathrm{m}}, \rho_{\mathrm{g}}\right]  \tag{32}\\
& \bar{\rho}_{\mathrm{g}}=\left(1-A_{\mathrm{t}}\right) \rho_{\mathrm{g}}+A_{\mathrm{t}} \rho_{\mathrm{m}}-i A_{\text {exch }}^{I}\left[\rho_{\mathrm{g}}, \rho_{\mathrm{m}}\right]
\end{align*}
$$

in which the ground and metastable states play a perfectly symmetric role. The nuclear orientation of each level acts as an apparent magnetic field for the other (of course, the total nuclear orientation is conserved whatever the directions of $\langle\mathbf{I}\rangle_{\mathrm{g}}$ and $\langle\mathbf{I}\rangle_{\mathrm{m}}$ ).
(ii) One can wonder whether any nuclear fictitious magnetic field exists for two colliding ${ }^{3} \mathrm{He}$ atoms both in the ground electronic state.

If, initially, the nuclear density operators of the two atoms are $\rho_{1}$ and $\rho_{2}$, a calculation similar to the preceding ones gives :

$$
\begin{align*}
\bar{\rho}=\frac{1}{2} & \int \mathrm{~d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \int \mathrm{d}^{3} k_{\mathrm{f}}\left\{S\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S^{*}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right) \rho_{1}+\right. \\
& \left.+S\left(\mathbf{k}_{\mathrm{f}},-\mathbf{k}_{\mathrm{i}}\right) S^{*}\left(\mathbf{k}_{\mathrm{f}},-\mathbf{k}_{\mathrm{i}}^{\prime}\right) \rho_{2}-S\left(\mathbf{k}_{\mathrm{f}},-\mathbf{k}_{\mathrm{i}}\right) S^{*}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right) \rho_{2} \rho_{1}-S\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S^{*}\left(\mathbf{k}_{\mathrm{f}},-\mathbf{k}_{\mathrm{i}}^{\prime}\right) \rho_{1} \rho_{2}\right\} . \tag{33}
\end{align*}
$$

Since $S$ is an unitary operator, we obtain :

$$
\begin{equation*}
\bar{\rho}=\frac{1}{2}\left(\rho_{1}+\rho_{2}\right)-\frac{1}{2}\left[C \rho_{2} \rho_{1}+C^{*} \rho_{1} \rho_{2}\right] \tag{34}
\end{equation*}
$$

with :

$$
\begin{align*}
C & =\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \int \mathrm{d}^{3} k_{\mathrm{f}} S\left(\mathbf{k}_{\mathrm{f}},-\mathbf{k}_{\mathrm{i}}\right) S^{*}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right) \\
& =\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right)\left\langle\mathbf{k}_{\mathrm{i}}^{\prime}\right| S^{\dagger} S\left|-\mathbf{k}_{\mathrm{i}}\right\rangle \tag{35}
\end{align*}
$$

But :

$$
\left\langle\mathbf{k}_{\mathrm{i}}^{\prime}\right| S^{\dagger} S\left|-\mathbf{k}_{\mathrm{i}}\right\rangle=\delta\left(\mathbf{k}_{\mathrm{i}}+\mathbf{k}_{\mathrm{i}}^{\prime}\right)
$$

so that :

$$
C=0 .
$$

This shows that there is no nuclear identity term in this case. Nevertheless, the cancellation of the non-
linear exchange term in $\rho_{1} \rho_{2}$ and $\rho_{2} \rho_{1}$ arises strictly from the summation over $\mathbf{k}_{\mathrm{f}}$. For each scattering direction $\hat{k}_{\mathrm{f}}$, nuclear identity effects do occur. Let us consider a beam experiment where atoms with a nuclear polarization $\langle\mathbf{I}\rangle_{1}$ collide with target atoms having a different nuclear polarization $\langle\mathbf{I}\rangle_{2}$. The nuclear orientation of the atoms scattered in a given direction $\hat{k}_{\mathrm{f}}$ is not simply a weighted average of $\langle\mathbf{I}\rangle_{1}$
and $\langle\mathbf{I}\rangle_{2}$, but also comprises other terms including a term in $\langle\mathbf{I}\rangle_{1} \times\langle\mathbf{I}\rangle_{2}$ which can be described by a effective spin hamiltonian. The coefficient of this term (and its sign) depends on the scattering direction. This last effect averages out only if one takes the summation over all possible final states (scattering in all directions or no scattering at all). For example, if only the spherical scattered wave is taken into account (the plane transmitted wave being ignored), nuclear identity effects change the internal variable density operator. These effects are studied in more detail in Appendix II of this article.

In the calculation of the diffusion coefficient in a dilute atomic gas, the integral over $\mathbf{k}_{f}$ generally includes geometrical factors like $1-\cos \theta$ (linear momentum transfer). All final states do not therefore play the same role in this case. One might then expect
that the nuclear identity terms in $\rho_{1} \rho_{2}$ and $\rho_{2} \rho_{1}$ could then remain to some extent. In other words, it seems possible that, in spin diffusion experiments in ${ }^{3} \mathrm{He}$ at low temperature, the evolution of nuclear magnetization is modified by nuclear identity effects related to the effective hamiltonian discussed in the present article.

## 3. Metastability exchange with depolarization. -

 Let us now study how the preceding equations must be modified when the collision does not completely conserve the electronic angular momentum $\mathbf{J}$.3.1 EVOLUTION OF THE DENSITY OPERATORS. Since the quantum number $M$ can now be changed during the collision, equations (1.a) and (1.b) have to be replaced by :

$$
\begin{equation*}
\left\langle 1: \mathbf{k}_{\mathrm{f}}, \mathrm{~g}, m_{I} ; 2:-\mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}^{\prime}, M\right| S\left|1: \mathbf{k}_{\mathrm{i}}, \mathrm{~g}, m_{I}^{\prime \prime} ; 2:-\mathbf{k}_{\mathrm{i}}, \mathrm{e}, m_{I}^{\prime \prime \prime} M^{\prime}\right\rangle=\delta_{m_{I} m_{I}^{\prime \prime}} \delta_{m_{I}^{\prime} m_{I}^{\prime \prime}} S_{\mathrm{d}}^{M M^{\prime}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathbf{i}}\right) \tag{36.a}
\end{equation*}
$$

(we still assume a complete inertia of the nuclear spin) and :

$$
\begin{equation*}
\left\langle 1: \mathbf{k}_{\mathrm{f}}, \mathrm{e}, m_{I}, M ; 2:-\mathbf{k}_{\mathrm{f}}, \mathrm{~g}, m_{I}^{\prime}\right| S\left|1: \mathbf{k}_{\mathrm{i}}, \mathrm{~g}, m_{I}^{\prime \prime} ; 2:-\mathbf{k}_{\mathrm{i}}, \mathrm{e}, m_{I}^{\prime \prime \prime} M^{\prime}\right\rangle=\delta_{m_{\mathrm{I}} m_{I}^{\prime \prime}} \delta_{m_{I}^{\prime} m_{I}^{\prime \prime}} S_{\mathrm{t}}^{M M^{\prime}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) . \tag{36.b}
\end{equation*}
$$

The density operator $\bar{\rho}_{\mathrm{m}}$ describing the internal variables of the metastable atom after collision is still given by (18) when the two nuclei are identical. We now have to introduce the coefficients $A_{\mathrm{d}}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)$ and $A_{\mathrm{t}}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)$ defined by :

$$
\begin{equation*}
A_{\mathrm{d}, \mathrm{t}}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathbf{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \int \mathrm{d}^{3} k_{\mathrm{f}} S_{\mathrm{d}, \mathrm{t}}^{M M^{\prime \prime}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S_{\mathrm{d}, \mathrm{t}}^{* M^{\prime} M^{\prime \prime \prime}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right) \tag{37}
\end{equation*}
$$

The terms in (18) containing either no $P_{n}$ operator or two such operators can then be written :

$$
\begin{aligned}
& \sum_{M^{\prime \prime} M^{\prime \prime \prime}}\left\{A_{\mathrm{d}}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)\left\langle m_{I}, M^{\prime \prime}\right| \rho_{\mathrm{m}}\left|m_{I}^{\prime}, M^{\prime \prime \prime}\right\rangle+\right. \\
&\left.+A_{\mathrm{t}}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)\left\langle m_{I}, M^{\prime \prime}\right| \rho_{\mathrm{g}} \otimes \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}\left|m_{I}^{\prime}, M^{\prime \prime \prime}\right\rangle\right\}
\end{aligned}
$$

The terms containing one $P_{\mathrm{n}}$ operator depend on the coefficients :

$$
\begin{equation*}
\bar{C}_{I}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathbf{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathbf{i}}^{\prime}\right) \int \mathrm{d}^{3} k_{\mathrm{f}} S_{\mathrm{d}}^{M M^{\prime \prime}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S_{\mathrm{t}}^{* M^{\prime} M^{\prime \prime \prime}}\left(-\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right) \tag{38}
\end{equation*}
$$

and, finally, we obtain :

$$
\begin{align*}
\left\langle m_{I}, M\right| \bar{\rho}_{\mathrm{m}}\left|m_{I}^{\prime}, M^{\prime}\right\rangle=\sum_{M^{\prime \prime} M^{\prime \prime}}\{ & A_{\mathrm{d}}\left(M, M^{\prime} ; M^{\prime \prime} M^{\prime \prime \prime}\right)\left\langle m_{I}, M^{\prime \prime}\right| \rho_{\mathrm{m}}\left|m_{I}^{\prime}, M^{\prime \prime \prime}\right\rangle+ \\
& +A_{\mathrm{t}}\left(M, M^{\prime} ; M^{\prime \prime} M^{\prime \prime \prime}\right)\left\langle m_{I}, M^{\prime \prime}\right| \rho_{\mathrm{g}} \otimes \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}\left|m_{I}^{\prime}, M^{\prime \prime \prime}\right\rangle \\
& -\bar{C}_{I}\left(M, M^{\prime} ; M^{\prime \prime} M^{\prime \prime \prime}\right)\left\langle m_{I}, M^{\prime \prime}\right| \rho_{\mathrm{m}} \times\left(\rho_{\mathrm{g}} \otimes \mathbb{1}_{J}\right)\left|m_{I}^{\prime}, M^{\prime \prime \prime}\right\rangle \\
& \left.-\bar{C}_{I}^{*}\left(M^{\prime}, M ; M^{\prime \prime \prime} M^{\prime \prime}\right)\left\langle m_{I}, M^{\prime \prime}\right|\left(\rho_{\mathrm{g}} \otimes \mathbb{1}_{J}\right) \times \rho_{\mathrm{m}}\left|m_{I}^{\prime}, M^{\prime \prime \prime}\right\rangle\right\} . \tag{39}
\end{align*}
$$

The same kind of calculation gives the density operator of the atom in the ground state after collision :

$$
\begin{align*}
\left\langle m_{I}\right| \bar{\rho}_{\mathrm{g}}\left|m_{I}^{\prime}\right\rangle & =\left\langle m_{I}\right| \rho_{\mathrm{g}}\left|m_{I}^{\prime}\right\rangle \sum_{M^{\prime \prime} M^{\prime \prime \prime}}\left\langle M^{\prime \prime}\right| \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}\left|M^{\prime \prime \prime}\right\rangle\left[\sum_{M} A_{\mathrm{d}}\left(M, M ; M^{\prime \prime} M^{\prime \prime \prime}\right)\right]+ \\
& +\sum_{M^{\prime \prime} M^{\prime \prime \prime}}\left\langle m_{I} M^{\prime \prime}\right| \rho_{\mathrm{m}}\left|m_{I}^{\prime} M^{\prime \prime \prime}\right\rangle\left[\sum_{M} A_{\mathrm{t}}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right)\right]-\left\langle m_{I}\right| \rho_{\mathrm{g}} \bar{E}_{I}+\bar{E}_{I}^{\dagger} \rho_{\mathrm{g}}\left|m_{I}^{\prime}\right\rangle \tag{40}
\end{align*}
$$

where the operator $\bar{E}_{I}$ acting on the nuclear variables is defined by :

$$
\begin{equation*}
\left\langle m_{I}\right| \bar{E}_{I}\left|m_{I}^{\prime}\right\rangle=\sum_{M^{\prime \prime} M^{\prime \prime \prime}}\left\langle m_{I} M^{\prime \prime}\right| \rho_{\mathrm{m}}\left|m_{I}^{\prime} M^{\prime \prime \prime}\right\rangle \times\left(\sum_{M} \bar{C}_{I}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right)\right) . \tag{41.a}
\end{equation*}
$$

Equivalently, one can write :

$$
\begin{equation*}
\bar{E}_{I}=\operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}} K_{J}\right\} \tag{41.b}
\end{equation*}
$$

with :

$$
\begin{equation*}
\left\langle m_{I} M^{\prime}\right| K_{J}\left|m_{I}^{\prime} M^{\prime \prime}\right\rangle=\delta_{m_{I} m_{I}^{\prime}} \times \sum_{M} \bar{C}_{I}\left(M, M ; M^{\prime \prime}, M^{\prime}\right) . \tag{42}
\end{equation*}
$$

The operator $K_{J}$ acts only on the $\mathbf{J}$ variables.
From definition (37) of $A_{\mathrm{d}}$ and $A_{\mathrm{t}}$, one obtains :

$$
\begin{equation*}
A_{\mathrm{d}, \mathrm{t}}\left(M, M^{\prime} ; M^{\prime \prime} M^{\prime \prime \prime}\right)=A_{\mathrm{d}, \mathrm{t}}^{*}\left(M^{\prime}, M ; M^{\prime \prime \prime} M^{\prime \prime}\right) . \tag{43}
\end{equation*}
$$

This relation and (39) imply that :

$$
\begin{equation*}
\left\langle m_{I}^{\prime}, M^{\prime}\right| \bar{\rho}_{\mathrm{m}}\left|m_{I} M\right\rangle=\left\langle m_{I}, M\right| \bar{\rho}_{\mathrm{m}}\left|m_{I}^{\prime} M^{\prime}\right\rangle^{*} \tag{44}
\end{equation*}
$$

and we check that $\rho_{\mathrm{m}}$ is an hermitian operator (the same can easily be done for $\rho_{\mathrm{g}}$ ).
From the unitary character of the $S$ matrix, one can show that :

$$
\begin{equation*}
\sum_{M}\left\{A_{\mathrm{d}}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right)+A_{\mathrm{t}}\left(M, M ; M^{\prime \prime} M^{\prime \prime \prime}\right)\right\}=\delta_{M^{\prime \prime} M^{\prime \prime \prime}} \tag{45.a}
\end{equation*}
$$

and :

$$
\begin{equation*}
\sum_{M}\left\{\bar{C}_{I}\left(M, M ; M^{\prime \prime} M^{\prime \prime \prime}\right)+\bar{C}_{I}^{*}\left(M, M ; M^{\prime \prime \prime}, M^{\prime \prime}\right)\right\}=0 . \tag{45.b}
\end{equation*}
$$

Combining these equations with (39) and (40), we obtain :

$$
\begin{align*}
\operatorname{Tr}\left\{\bar{\rho}_{\mathrm{m}}\right\}= & \sum_{m_{I} M}\left\langle m_{I}, M\right| \bar{\rho}_{\mathrm{m}}\left|m_{I}, M\right\rangle \\
= & \sum_{M M^{\prime \prime M^{\prime \prime \prime}}}\left\{A_{\mathrm{d}}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right)\left\langle M^{\prime \prime}\right| \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}\left|M^{\prime \prime \prime}\right\rangle+\right. \\
& \quad+A_{\mathrm{t}}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right)\left\langle M^{\prime \prime}\right| \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}\left|M^{\prime \prime \prime}\right\rangle \\
& \quad-\bar{C}_{I}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right)\left\langle M^{\prime \prime}\right| \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}} \times\left(\rho_{\mathrm{g}} \otimes \mathbb{1}_{J}\right)\right\}\left|M^{\prime \prime \prime}\right\rangle \\
& \left.\quad-\bar{C}_{I}^{*}\left(M, M ; M^{\prime \prime \prime}, M^{\prime \prime}\right)\left\langle M^{\prime \prime}\right| \operatorname{Tr}_{I}\left\{\left(\rho_{\mathrm{g}} \otimes \mathbb{1}_{J}\right) \times \rho_{\mathrm{m}}\right\}\left|M^{\prime \prime \prime}\right\rangle\right\} \\
= & \sum_{M^{\prime \prime}}\left\langle M^{\prime \prime}\right| \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}\left|M^{\prime \prime}\right\rangle=1 . \tag{46}
\end{align*}
$$

We have used the fact that, since $\rho_{\mathrm{g}} \otimes{\tau_{J}}$ is an operator acting only in the I variable state :

$$
\operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}} \times\left(\rho_{\mathrm{g}} \otimes \mathbb{1}_{J}\right)\right\}=\operatorname{Tr}_{I}\left\{\left(\rho_{\mathrm{g}} \otimes \mathbb{1}_{J}\right) \times \rho_{\mathrm{m}}\right\}
$$

Equation (45.b) is actually equivalent to :

$$
\begin{equation*}
K_{J}+K_{J}^{\dagger}=0 \tag{47.a}
\end{equation*}
$$

or :

$$
\begin{equation*}
\bar{E}_{I}+\bar{E}_{I}^{\dagger}=0 . \tag{47.b}
\end{equation*}
$$

Thus, if we set :

$$
\begin{equation*}
\bar{H}_{I}=\bar{H}_{I}^{\dagger}=i \bar{E}_{I} \tag{48}
\end{equation*}
$$

the last term in the right hand side of (40) takes the form :

$$
\begin{equation*}
i\left\langle m_{I}\right|\left[\rho_{\mathrm{g}}, \bar{H}_{I}\right]\left|m_{I}^{\prime}\right\rangle \tag{49}
\end{equation*}
$$

( $\bar{H}_{I}$ plays the role of an effective hamiltonian arising from nuclear identity.) Using this last result, (40) and (45.a), it is easy to check that :

$$
\begin{equation*}
\operatorname{Tr}\left\{\bar{\rho}_{\mathrm{g}}\right\}=1 \tag{50}
\end{equation*}
$$

Until now, we have not made use of rotational invariance. If the Oz quantization axis is parallel to
the initial collision axis [defined by $u(\mathbf{k})$ ], cylindrical symmetry around Oz imposes that :

$$
A_{\mathrm{d}}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right) \propto \delta_{M+M^{\prime \prime \prime} \cdot M^{\prime}+M^{\prime \prime}}
$$

and similar equalities for $A_{\mathrm{t}}$ and $\bar{C}_{I}$ : only coherences associated with the same value of the difference $M-M^{\prime}$ are then coupled by the collision.
In most optical pumping experiments, collisions occur in all directions of space and a full rotational invariance is obtained. The values of $A_{\mathrm{d}, \mathrm{t}}$ and $\bar{C}_{I}$ must then be averaged over all possible initial relative velocities of the atoms, and it is convenient to expand the density operators on a basis formed by irreducible tensor operators [20]. One then obtains, for any choice of the $\mathrm{O} z$ quantization axis [13, 2] :

$$
\begin{align*}
& \quad A_{\mathrm{d}, \mathrm{t}}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)=\sum_{k, q}(-1)^{M-M^{\prime \prime}} \alpha_{\mathrm{d}, \mathrm{t}}^{k} \times \\
& \times\left\langle J J M-M^{\prime} \mid k q\right\rangle\left\langle J J M^{\prime \prime}-M^{\prime \prime \prime} \mid k q\right\rangle  \tag{51.a}\\
& \\
& \bar{C}_{I}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)=\sum_{k, q}(-1)^{M-M^{\prime \prime}} \bar{\beta}_{I}^{k} \times
\end{align*}
$$

$$
\begin{equation*}
\times\left\langle J J M-M^{\prime} \mid k q\right\rangle\left\langle J J M^{\prime \prime}-M^{\prime \prime \prime} \mid k q\right\rangle . \tag{51.b}
\end{equation*}
$$

Equation (43) is then equivalent to imposing the reality of all coefficients $\alpha_{\mathrm{d}, \mathrm{t}}^{k}$ (but the $\beta_{I}^{k}$ 's may be complex). Replacing the number $(-1)^{M-M^{\prime \prime}}$ by :
$(-1)^{M-M^{\prime \prime}}=\sqrt{2 J+1}(-1)^{J-M^{\prime \prime}}\langle J J M-M \mid 00\rangle$
in equations (51) and using the sum rule for the Clebsch-Gordan coefficients, one can show that :

$$
\begin{align*}
& \sum_{M} A_{\mathrm{d}, \mathrm{t}}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right)=\delta_{M^{\prime \prime} M^{\prime \prime \prime}} \alpha_{\mathrm{d}, \mathrm{t}}^{0}  \tag{53.a}\\
& \sum_{M} \bar{C}_{I}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right)=\delta_{M^{\prime \prime} M^{\prime \prime}} \beta_{I}^{0} \tag{53.b}
\end{align*}
$$

(the latter equation implies that $K_{J}$ is proportional to unity).

The two unitarity relations (45) then give :

$$
\left\{\begin{array}{l}
\alpha_{\mathrm{d}}^{0}+\alpha_{\mathrm{I}}^{0}=1  \tag{54.a}\\
\beta_{I}^{0}+\beta_{I}^{0 *}=0
\end{array}\right.
$$

Relations (51) also imply that :

$$
\begin{align*}
& A_{\mathrm{d}, \mathrm{t}}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)=A_{\mathrm{d}, \mathrm{t}}\left(M^{\prime \prime}, M^{\prime \prime \prime} ; M, M^{\prime}\right)  \tag{55.a}\\
& A_{\mathrm{d}, \mathrm{t}}\left(M, M^{\prime} ; M^{\prime \prime} M^{\prime \prime \prime}\right)=A_{\mathrm{d}, \mathrm{t}}\left(M^{\prime}, M ; M^{\prime \prime \prime}, M^{\prime \prime}\right) \tag{55.b}
\end{align*}
$$

as well as similar equalities for the $\bar{C}_{I}$.
When all coefficients $\alpha_{\mathrm{d}}^{k}$ are equal to $\alpha_{\mathrm{d}}^{0}$, all coefficients $\alpha_{t}^{k}$ equal to $\alpha_{t}^{0}$ and all coefficients $\beta_{I}^{k}$ equal to $\beta_{I}^{0}$ (which is pure imaginary), it is then easy to see on ( $51 . a$ ) and ( $51 . b$ ) that the coefficients $A_{\mathrm{d}, \mathrm{t}}$ and $\bar{C}_{I}$ are different from zero only if $M=M^{\prime \prime}, M^{\prime}=M^{\prime \prime \prime}$, and independent of $M$ and $M^{\prime}$. This corresponds to the case studied in the preceding section (helium metastability exchange).
3.2 Discussion. - We shall first study the evolution of the ground state density operator, then the evolution of the metastable state. One notices that (40) has a simpler structure than (39) : for example, for the ground state evolution, only coefficients $A$ and $\bar{C}_{I}$ with $M=M^{\prime}$ play a role, and they are always summed over $M$.
(i) Ground state evolution.

The evolution of $\rho_{\mathrm{g}}$ is, according to (40), due to the sum of three contributions : a direct term $\left(\bar{\rho}_{\mathrm{g}}\right)_{\mathrm{d}}$, a transfer term $\left(\bar{\rho}_{\mathrm{g}}\right)_{t}$, and a term $\left(\bar{\rho}_{\mathrm{g}}\right)_{I}$ which can be described by an effective hamiltonian $\bar{H}_{I}$ defined by (41) and (48).

Direct term. - The structure of $\left(\bar{\rho}_{\mathrm{g}}\right)_{\mathrm{d}}$ is very simple : it is the product of $\rho_{\mathrm{g}}$, the unmodified ground state density operator before collision, by an electronic coefficient :

$$
\begin{align*}
\sum_{M^{\prime \prime} M^{\prime \prime \prime}}\left\langle M^{\prime \prime}\right| & \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}\left|M^{\prime \prime \prime}\right\rangle \times \\
& \times \sum_{M} A_{\mathrm{d}}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right) \tag{56}
\end{align*}
$$

This coefficient is nothing but the probability that no excitation transfer will occur during a collision between a metastable atom with $I=0$ (even isotope), having an internal density operator $\operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}$, and a ground state atom, when nuclear identity effects are ignored (the second atom may be a different isotope for example). Since the collision hamiltonian does not act on the I variables, this is a physically satisfying result [when rotational invariance is satisfied, this non-transfer probability is merely $\alpha_{\mathrm{d}}^{0}$ as can be shown from (53)].

Transfer term. - The term $\left(\bar{\rho}_{\mathrm{g}}\right)_{t}$ has a structure a little more complicated than $\left(\bar{\rho}_{\mathrm{g}}\right)_{\mathrm{d}}$. If one uses the rotation invariance equality ( $53 . a$ ), one can rewrite this term in the form :
$\left(\bar{\rho}_{\mathrm{g}}\right)_{t}=\alpha_{\mathrm{t}}^{0} \sum_{M^{\prime \prime}}\left\langle m_{I} M^{\prime \prime}\right| \rho_{\mathrm{m}}\left|m_{I}^{\prime} M^{\prime \prime}\right\rangle=\alpha_{\mathrm{t}}^{0} \operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}$
which corresponds to what we obtained in section 2 : after metastability exchange, the ground state density operator is merely the I variable density operator of the metastable atom before collision. Another case where an analogous result is obtained occurs when $\mathbf{I}$ and $\mathbf{J}$ are initially uncorrelated :

$$
\begin{equation*}
\rho_{\mathrm{m}}=\rho_{\mathrm{m}}^{I} \otimes \rho_{\mathrm{m}}^{J} \tag{57}
\end{equation*}
$$

Then :

$$
\begin{align*}
\left(\bar{g}_{\mathrm{g}}\right)_{\mathrm{t}}=\rho_{\mathrm{m}}^{I} \times \sum_{M^{\prime \prime} M^{\prime \prime \prime}} & \left.<M^{\prime \prime}\left|\rho_{\mathrm{m}}^{J}\right| M^{\prime \prime \prime}\right\rangle \times \\
& \times \sum_{M} A_{\mathrm{t}}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right) \tag{58}
\end{align*}
$$

In this case, the density operator is simply $\rho_{\mathrm{m}}^{I}$ multiplied by a coefficient similar to (56), which gives the probability that an excitation transfer will occur for an even isotope with internal density operator $\rho_{\mathrm{m}}^{J}$ (when nuclear identity effects are ignored).

Nevertheless, in the general case where I and $\mathbf{J}$ are correlated and no spherical average over the initial velocities can be taken (collision between atomic beams for example), equation (40) shows that the situation is more complex : $\left(\bar{\rho}_{\mathrm{g}}\right)_{\mathrm{t}}$ cannot be expressed as a function of $\operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}$. This result may seem very surprising at first sight. The physical explanation is that the transfer probability for an even isotope depends in general on the initial quantum number $M$. If $I$ and $J$ are correlated, the final state of $I$ after exchange may be different from the initial one. When, for example, the $|+\rangle$ state of $\mathbf{I}$ is correlated with a value of $M$ having a strong excitation transfer probability, the $|-\rangle$ state with a $M$ value with a low transfer probability, the final state of $I$ is more likely to be $\mid+>$ even if, initially, $I$ is unpolarized.

Nuclear identity term. - The remaining terms in (40), which are expressed in (49) as functions of $\bar{H}_{I}$, are a specific consequence of the nuclear identity. They actually have the properties already discussed in section 2 for a collision without action on the $\mathbf{J}$
variables. For example, if the metastable state density operator $\rho_{\mathrm{m}}$ is proportional to identity (no orientation, etc...), we obtain from (41.a) :

$$
\begin{align*}
\left\langle m_{I}\right| \bar{H}_{I}\left|m_{I}^{\prime}\right\rangle= & i\left\langle m_{I}\right| \bar{E}_{I}\left|m_{I}^{\prime}\right\rangle \\
= & \delta_{m_{I} m_{I}^{\prime}}(2 I+1)^{-1}(2 J+1)^{-1} \times \\
& \times \sum_{M M^{\prime \prime}} \bar{C}_{I}\left(M, M ; M^{\prime \prime} M^{\prime \prime}\right) \tag{59}
\end{align*}
$$

which shows that $\bar{H}_{I}$ can only shift the energy of all ground state sublevels by the same amount. The effect of $\bar{H}_{I}$ can then be ignored as far as the evolution of $\rho_{\mathrm{g}}$ is concerned.

When $\rho_{\mathrm{m}}$ is given by (57), that is when the $\mathbf{I}$ and $\mathbf{J}$ variables are uncorrelated, the fictitious hamiltonian is proportional to $\rho_{\mathrm{m}}^{I}$. This is also true, even when I and $\mathbf{J}$ are correlated, if rotational invariance can be used, since equation (53.b) gives the simple result :

$$
\begin{equation*}
\bar{H}_{I}=\left(i \beta_{I}^{0}\right) \operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}=\left(i \beta_{I}^{0}\right) \rho_{\mathrm{m}}^{I} \tag{60}
\end{equation*}
$$

[where the coefficient $\left(i \beta_{I}^{0}\right)$ is real according to (54.b)]. This result exactly coincides with what we obtained in section 2. It shows that the effective hamiltonian in the ground state, due to nuclear identity, does not depend at all on the depolarization, de-alignment, etc..., properties of the electronic collisions [as far as these collisions occur in all directions with the same probability and only one $J$ electronic level is involved]. We shall see below that the situation is less simple for the metastable state evolution.

In the general case where $\mathbf{I}$ and $\mathbf{J}$ are correlated and no rotational invariance is satisfied, equation (41) shows how the nuclear effective hamiltonian $H_{I}=i E_{I}$ depends on the whole density matrix $\rho_{\mathrm{m}}$ and not only on $\rho_{\mathrm{m}}^{\boldsymbol{I}}$.
(ii) Metastable state evolution.

The right hand side of (39) is the sum of three contributions : a direct term $\left(\bar{\rho}_{\mathrm{m}}\right)_{\mathrm{d}}$ depending on the coefficients $A_{\mathrm{d}}$, a transfer term $\left(\bar{\rho}_{\mathrm{m}}\right)_{\mathrm{t}}$ depending on the $A_{\mathrm{t}}$ 's and a term $\left(\rho_{\mathrm{m}}\right)_{\mathrm{I}}$ arising from nuclear identity which is function of the $\bar{C}_{I}$ coefficients.

Direct term. - The first term describes the effect of collisions in the excited states when all transfer processes are ignored. This term is obtained in the study of low energy collisions between atoms having different electronic levels [transfer processes are then negligible]. If rotation invariance is satisfied, it is convenient to write $\rho_{\mathrm{m}}$ in the form [12,13]:

$$
\begin{equation*}
\rho_{\mathrm{m}}=\sum_{k, q} \sum_{k^{\prime}, q^{\prime}} \rho_{q q^{\prime}}^{k k^{\prime}}\left[T_{q .}^{(k)}\right]_{I} \otimes\left[T_{q^{\prime}}^{\left(k^{\prime}\right)}\right]_{J} \tag{61}
\end{equation*}
$$

One can then show that $\left(\bar{\rho}_{\mathrm{m}}\right)_{\mathrm{d}}$ is obtained from $\rho_{\mathrm{m}}$ by replacing all the $\rho_{q q^{\prime}}^{\boldsymbol{k} k^{\prime}}$ by :

$$
\begin{equation*}
\left(\bar{\rho}_{q q^{\prime}}^{k k^{\prime}}\right)_{\mathbf{d}}=\alpha_{\mathbf{d}}^{k^{\prime}} \rho_{q q^{\prime}}^{k k^{\prime}} . \tag{62}
\end{equation*}
$$

This classical result expresses that $\mathbf{I}$ is not affected by the collision. It is also possible to evaluate the two partial density operators :

$$
\begin{align*}
& \left(\bar{\rho}_{\mathrm{m}}^{I}\right)_{\mathrm{d}}=\operatorname{Tr}_{J}\left\{\left(\bar{\rho}_{\mathrm{m}}\right)_{\mathrm{d}}\right\} \\
& \left(\bar{\rho}_{\mathrm{m}}^{J}\right)_{\mathrm{d}}=\operatorname{Tr}_{I}\left\{\left(\bar{\rho}_{\mathrm{m}}\right)_{\mathrm{d}}\right\} \tag{63.a}
\end{align*}
$$

Equation (39) shows that $\left(\bar{\rho}_{\mathrm{m}}^{J}\right)_{\mathrm{d}}$ has exactly the same form as for an even isotope ( $I=0$ ). This again expresses the fact that the collision only acts on the electronic variables. To evaluate $\left(\bar{\rho}_{\mathrm{m}}^{I}\right)_{\mathrm{d}}$, the rotational invariance equation (53.a) can be used and gives :

$$
\begin{equation*}
\left(\bar{\rho}_{\mathrm{m}}^{I}\right)_{\mathrm{d}}=\alpha_{\mathrm{d}}^{0} \operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\} \tag{64}
\end{equation*}
$$

which is physically satisfying for the same reason.
Nevertheless, when the collisions do not occur with the same probability in all directions, this result is no longer true. Although the expression for $\left(\bar{\rho}_{\mathrm{m}}^{J}\right)_{\mathrm{d}}$ is still completely independent of nuclear variables, no simple expression like (64) can be found for $\left(\bar{\rho}_{\mathrm{m}}^{I}\right)_{\mathrm{d}}$ in general. The physical reason is the same as for the term $\left(\bar{\rho}_{\mathrm{g}}\right)_{\mathrm{t}}$ discussed above : when $\mathbf{I}$ and $\mathbf{J}$ are correlated and when the probability for a direct process depends on the direction of $\mathbf{J}$, after such a process, the state of I can be modified. To confirm this interpretation, one can easily check that, when equation (57) is satisfied, that is when $\mathbf{I}$ and $\mathbf{J}$ are uncorrelated, a result similar to (64) is recovered (even in the absence of rotational invariance) :

$$
\begin{align*}
\left(\bar{\rho}_{\mathrm{m}}^{I}\right)_{\mathrm{d}} & =\rho_{\mathrm{m}}^{I} \times \\
& \times \sum_{M M^{\prime \prime} M^{\prime \prime}} A_{\mathrm{d}}\left(M, M ; M^{\prime \prime} M^{\prime \prime \prime}\right)\left\langle M^{\prime \prime}\right| \rho_{\mathrm{m}}^{J}\left|M^{\prime \prime \prime}\right\rangle . \tag{65}
\end{align*}
$$

Also, it is physically clear that the total density operator of the nuclear spin of atom 2 (we assume here that the nuclei are distinguishable) cannot be modified if one includes all possible final states. This can also be checked on equations (39) and (40) since the unitarity relationship (45.a) implies that :

$$
\begin{array}{r}
\left\langle m_{I}\right|\left[\left(\bar{\rho}_{\mathrm{g}}\right)_{\mathrm{t}}+\left(\bar{\rho}_{\mathrm{m}}^{I}\right)_{\mathrm{d}}\right]\left|m_{I}^{\prime}\right\rangle=\sum_{M M^{\prime \prime} M^{\prime \prime \prime}}\left\langle m_{I} M^{\prime \prime}\right| \rho_{\mathrm{m}}\left|m_{I}^{\prime} M^{\prime \prime \prime}\right\rangle \times\left[A_{\mathrm{d}}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right)+A_{\mathrm{t}}\left(M, M ; M^{\prime \prime}, M^{\prime \prime \prime}\right)\right]= \\
=\sum_{M^{\prime \prime}}\left\langle m_{I} M^{\prime \prime}\right| \rho_{\mathrm{m}}\left|m_{I}^{\prime} M^{\prime \prime}\right\rangle=\left\langle m_{I}\right| \operatorname{Tr}_{J}\left\{\rho_{\mathrm{m}}\right\}\left|m_{I}^{\prime}\right\rangle \tag{66}
\end{array}
$$

Transfer term. - The term $\left(\bar{\rho}_{\mathrm{m}}\right)_{\mathrm{t}}$ has a simpler structure than $\left(\bar{\rho}_{\mathrm{m}}\right)_{\mathrm{d}}$ and can be written as a tensor product :

$$
\begin{equation*}
\left(\bar{\rho}_{\mathrm{m}}\right)_{\mathrm{t}}=\rho_{\mathrm{g}} \otimes\left(\bar{\rho}_{\mathrm{m}}^{J}\right)_{\mathrm{t}} \tag{67.a}
\end{equation*}
$$

with :
$\langle M|\left(\bar{\rho}_{\mathrm{m}}^{J}\right)_{\mathrm{t}}\left|M^{\prime}\right\rangle=\sum_{M^{\prime \prime} M^{\prime \prime \prime}}\left\langle M^{\prime \prime}\right| \operatorname{Tr}_{I}\left\{\rho_{\mathrm{m}}\right\}\left|M^{\prime \prime \prime}\right\rangle \times$

Thus, after a transfer process, I and $\mathbf{J}$ are completely uncorrelated, and the density operator $\left(\bar{\rho}_{\mathrm{m}}^{J}\right)_{\mathrm{t}}$ describing the state of the $\mathbf{J}$ variables is the same as for an even isotope with $I=0$ (when nuclear identity effects are ignored).

Nuclear identity terms. - The most interesting terms in the right hand side of (39) are probably the nuclear identity terms in $\bar{C}_{I}$ and $\bar{C}_{I}^{*}$. It can be first checked that, when $\mathbf{I}$ and $\mathbf{J}$ are uncorrelated, that is when $\rho_{\mathrm{m}}$ is given by (57), these terms take the form :

$$
\begin{equation*}
-\left[\rho_{\mathrm{m}}^{I} \rho_{\mathrm{g}}\right] \otimes\left(\bar{Q}_{\mathrm{m}}^{J}\right)-\left[\rho_{\mathrm{g}} \rho_{\mathrm{m}}^{I}\right] \otimes\left(Q_{\mathrm{m}}^{J}\right)^{\dagger} \tag{68.a}
\end{equation*}
$$

where the purely electronic operator $\bar{Q}_{\mathrm{m}}^{J}$ is defined by :

$$
\begin{aligned}
\langle M| \bar{Q}_{\mathrm{m}}^{J}\left|M^{\prime}\right\rangle=\sum_{M^{\prime \prime} M^{\prime \prime \prime}} & \bar{C}_{I}\left(M, M^{\prime} ; M^{\prime \prime} M^{\prime \prime \prime}\right) \times \\
& \times\left\langle M^{\prime \prime}\right| \rho_{\mathrm{m}}^{J}\left|M^{\prime \prime \prime}\right\rangle .
\end{aligned}
$$

The presence of the products $\left[\rho_{\mathrm{m}}^{I} \rho_{\mathrm{g}}\right]$ and $\left[\rho_{\mathrm{g}} \rho_{\mathrm{m}}^{I}\right.$ ] implies that the nuclear identity term vanishes each time the two nuclear spins are in two orthogonal spin states (particles distinguishable by their spin directions). For an even isotope, ( $68 . a$ ) becomes :

$$
\begin{equation*}
\left(\bar{\rho}_{\mathrm{m}}^{J}\right)_{\mathrm{exch}}=\bar{Q}_{\mathrm{m}}^{J}+\bar{Q}_{\mathrm{m}}^{J \dagger} \tag{69}
\end{equation*}
$$

When $I \neq 0$, the operator written in (68.a) is not the tensor product of $\left(\bar{\rho}_{\mathrm{m}}^{J}\right)_{\mathrm{exch}}^{I=0}$ by a nuclear operator, except if $\rho_{\mathrm{m}}^{I}$ and $\rho_{\mathrm{g}}$ commute with each other. Since initially $\mathbf{I}$ and $\mathbf{J}$ were supposed to be completely uncorrelated, and the collision hamiltonian acts only on $\mathbf{J}$, it may seem very surprising that some correlation between $I$ and $\mathbf{J}$ has been introduced in the atom which is metastable after collision. The physical explanation is that the initial directions of the two nuclear spins determine the way the two electronic processes (direct and transfer) interfere in the final state. Of course, this correlation does not change the trace of the density matrix, since (45.b) implies that :

$$
\begin{equation*}
\operatorname{Tr}\left\{\left(\bar{\rho}_{\mathrm{m}}^{J}\right)_{\mathrm{exch}}\right\}=0 \tag{70}
\end{equation*}
$$

It is also interesting to study how the two partial traces $\rho_{\mathrm{m}}^{I}$ and $\rho_{\mathrm{m}}^{J}$ are affected by the nuclear identity terms, still supposing no initial correlation between I and $\mathbf{J}$ variables. Equation ( $68 . a$ ) gives, for the I density operator, a contribution :

$$
\begin{equation*}
\bar{\delta}_{\text {exch }} \rho_{\mathrm{m}}^{I} \rho_{\mathrm{g}}+\bar{\delta}_{\mathrm{exch}}^{*} \rho_{\mathrm{g}} \rho_{\mathrm{m}}^{I} \tag{71}
\end{equation*}
$$

with :

$$
\begin{equation*}
\bar{\delta}_{\mathrm{exch}}=\operatorname{Tr}\left\{\bar{Q}_{\mathrm{m}}^{J}\right\} \tag{72}
\end{equation*}
$$

Equation (45.b) shows that $\bar{\delta}_{\text {exch }}$ is pure imaginary, so that (71) reduces to a commutator $\left[\rho_{\mathrm{m}}^{I}, \rho_{\mathrm{g}}\right.$ ]. On the other hand, the $\mathbf{J}$ variable density operator contains a contribution :

$$
\begin{equation*}
\operatorname{Tr}\left\{\rho_{\mathrm{m}}^{I} \rho_{\mathrm{g}}\right\}\left[\left(\bar{Q}_{\mathrm{m}}^{J}\right)+\left(\bar{Q}_{\mathrm{m}}^{J}\right)^{\dagger}\right] \tag{73}
\end{equation*}
$$

The $\mathbf{J}$ variables are thus affected and this clearly shows that, in general, nuclear identity effects cannot be described by an effective hamiltonian acting only on the nuclear spin.

If rotational invariance is satisfied, we can simplify the previous results. Equations ( $51 . b$ ) and ( $68 . b$ ) show that $\bar{Q}_{\mathrm{m}}^{J}$ is simply obtained from $\rho_{\mathrm{m}}^{J}$ by multiplying each of the $k, q$ tensor components of this operator by $\beta_{I}^{k}$. If, in addition, all coefficients $\beta_{I}^{k}$ are equal (as in helium metastability exchange), we have :

$$
Q_{\mathrm{m}}^{J}=-i\left(i \beta_{\mathrm{I}}^{0}\right) \rho_{\mathrm{m}}^{J}
$$

$\left[\left(i \beta_{I}^{0}\right)\right.$ is real $\left.; \mathrm{cf} .(54 . b)\right]$ and (68a) becomes equal to :

$$
\begin{equation*}
i\left(i \beta_{I}^{0}\right)\left[\rho_{\mathrm{m}}^{I} \otimes \rho_{\mathrm{m}}^{J}, \rho_{\mathrm{g}}\right]=i\left(i \beta_{I}^{0}\right)\left[\rho_{\mathrm{m}}, \rho_{\mathrm{g}}\right] \tag{74}
\end{equation*}
$$

We know from section 2 that, when the collision does not affect the $\mathbf{J}$ variables, this result remains valid even if $\rho_{\mathrm{m}}$ is not a tensor product of $\rho_{\mathrm{m}}^{I}$ and $\rho_{\mathrm{m}}^{J}$ and rotational invariance is not satisfied.

Let us finally study the general case where I and J are correlated. It is then convenient to rewrite the terms in $\bar{C}_{I}$ and $\bar{C}_{I}^{*}$ of equation (39) in a different form. If we introduce the real coefficients $X_{I}$ and $Y_{I}$ :

$$
\begin{equation*}
\bar{C}_{I}\left(M, M^{\prime}, M^{\prime \prime}, M^{\prime \prime \prime}\right)=X_{I}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)+i Y_{I}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right) \tag{75}
\end{equation*}
$$

and set :

$$
\begin{align*}
& 2 X_{I}^{ \pm}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)=X_{I}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right) \pm X_{I}\left(M^{\prime}, M ; M^{\prime \prime \prime}, M^{\prime \prime}\right) \\
& 2 Y_{I}^{ \pm}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)=Y_{I}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right) \pm Y_{I}\left(M^{\prime}, M ; M^{\prime \prime \prime}, M^{\prime \prime}\right) \tag{76}
\end{align*}
$$

the terms in $\bar{C}_{I}$ and $\bar{C}_{I}^{*}$ become :

$$
\begin{align*}
& -\sum_{M^{\prime \prime} M^{\prime \prime \prime}}\left\{X_{I}^{+}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)+i Y_{I}^{-}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)\right\}\left\langle m_{I} M^{\prime \prime}\right|\left[\rho_{\mathrm{m}}, \rho_{\mathrm{g}} \otimes \mathbb{1}_{J}\right]_{+}\left|m_{I}^{\prime} M^{\prime \prime \prime}\right\rangle \\
& -\sum_{M^{\prime \prime} M^{\prime \prime \prime}}\left\{X_{I}^{-}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)+i Y_{I}^{+}\left(M, M^{\prime} ; M^{\prime \prime}, M^{\prime \prime \prime}\right)\right\}\left\langle m_{I} M^{\prime \prime}\right|\left[\rho_{\mathrm{m}}, \rho_{\mathrm{g}} \otimes \mathbb{1}_{J}\right]\left|m_{I}^{\prime} M^{\prime \prime \prime}\right\rangle \tag{77}
\end{align*}
$$

For an even isotope with $I=0$, only the first term, proportional to $X_{I}^{+}+i Y_{I}^{-}$, remains in this equation. This remains true for an odd isotope when the ground state has no orientation, alignment, etc.... The term in $X_{I}^{-}+i Y_{I}^{+}$can actually be neglected each time these observables have low values in both ground and metastable states [they are of second order]. This is very reminiscent of metastability exchange collisions without electronic depolarization. In the same way, it is easy to check that the term in $X_{I}^{-}+i Y_{I}^{+}$changes the I variable density operator after collision, but does not change the $J$ variable density operator.
When rotational invariance is satisfied, equation (51.b) implies that :

$$
\begin{equation*}
X_{I}^{-}=Y_{I}^{-}=0 \tag{78}
\end{equation*}
$$

If, in addition, the collision does not act on the $J$ variables, all coefficients $\bar{\beta}_{I}^{k}$ are equal to $\bar{\beta}_{I}^{0}$ which is pure imaginary, so that :

$$
\begin{equation*}
X_{I}^{+}=0 \tag{79}
\end{equation*}
$$

In this case, only the last term in (77) subsists, and we find again the results of section 2.

Rotational invariance equation (51.b) can also be directly used with (39) to show that the nuclear exchange terms can be obtained by replacing in expansion (61) of $\rho_{\mathrm{m}}$ each operator :

$$
\begin{equation*}
\left[T_{q}^{(k)}\right]_{I} \otimes\left[T_{q^{\prime}}^{\left(k^{\prime}\right)}\right]_{J} \tag{80.a}
\end{equation*}
$$

by :

$$
\begin{align*}
& -\left\{\left[T_{q}^{(k)}\right]_{I} \times \rho_{\mathrm{g}}\right\} \otimes\left\{\bar{\beta}_{I}^{k^{\prime}}\left[T_{q^{\prime}}^{\left(k^{\prime}\right)}\right]_{J}\right\}- \\
& \quad-\left\{\left(\bar{\beta}_{I}^{k^{\prime}}\right)^{*}\left[T_{q^{\prime}}^{\left(k^{\prime}\right)}\right]_{J}^{+}\right\} \otimes\left\{\rho_{\mathrm{g}} \times\left[T_{q}^{(k)}\right]_{I}\right\} . \tag{80.b}
\end{align*}
$$

The comparison with equation (61) for example shows that nuclear identity terms give a more complex (non-linear) structure to the final density operator $\bar{\rho}_{\mathrm{m}}$, even when rotational invariance is included.
they have never been included in the interpretation of experimental data with the $2{ }^{3} \mathrm{~S}_{1}$ optical pumping for example. Nevertheless, we believe that the considerations given in this article show that nuclear identity effects can become important, in particular in low temperature experiments. The realization of a c.w. tunable laser at $\lambda=1.08 \mu$ should allow obtaining high nuclear polarization to be induced, enabling identity effects to be observed. In the presence of electronic depolarization due to the collisions, some results remain unchanged (ground state effective hamiltonian for example). On the other hand, the way nuclear orientations in the ground state affect the evolution of the electronic density operator $\rho_{\mathrm{m}}^{J}$, through nuclear identity is not obvious and requires some care in its evaluation.

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## APPENDIX I

Phase shift calculation of the coefficients $A_{t}$ and $\boldsymbol{A}_{\text {exch. }}^{I}$ - This appendix is the analogue of the Appendix to reference [1], but applied to the case of metastability exchange collisions instead of spin exchange. We consider here two (fictitious) particles having all properties of the nuclei of the colliding atoms, but spin and indistinguishability. The spins of the electrons are also ignored. The reasoning is actually almost identical to the one in [1], and we can define states of the internal electronic variables by :

$$
\begin{equation*}
|G, U\rangle=\frac{1}{\sqrt{2}}[|1: \mathrm{g} ; 2: \mathrm{e}\rangle \pm|1: \mathrm{e} ; 2: \mathrm{g}\rangle] \tag{B.1}
\end{equation*}
$$

For such electronic states and for fixed positions of the nuclei, the atomic potential curves are well defined [ $V_{\mathrm{g}}$ and $V_{\mathrm{u}}$ ]. Many calculations of these potentials can be found in the literature (refs. [6], [15], [21-27]). Let us set :
4. Conclusion. - There are practical situations where nuclear identity effects do not strongly modify the properties of metastability exchange collisions, which are relevant in optical pumping experiments. This fully justifies the fact that, to our knowledge,

$$
\begin{equation*}
S_{\mathrm{g}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right)=\left[\left\langle 1: k_{\mathrm{f}} ; 2:-\mathbf{k}_{\mathrm{f}}\right| \otimes\langle G|\right] S\left[|G\rangle \times\left|1: \mathbf{k}_{\mathrm{i}} ; 2:-\mathbf{k}_{\mathrm{i}}\right\rangle\right] \tag{B.2}
\end{equation*}
$$

and :

$$
\begin{equation*}
S_{\mathrm{u}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathbf{i}}\right)=\left[\left\langle 1: \mathbf{k}_{\mathrm{f}} ; 2:-\mathbf{k}_{\mathrm{f}}\right| \otimes\langle U|\right] S\left[|U\rangle \times\left|1: \mathbf{k}_{\mathrm{i}} ; 2:-\mathbf{k}_{\mathrm{i}}\right\rangle\right] \tag{B.3}
\end{equation*}
$$

If $\delta_{l}^{\mathrm{g}}$ and $\delta_{l}^{\mathrm{u}}$ denote the phase shifts respectively associated with $V_{\mathrm{g}}$ and $V_{\mathrm{u}}$, one can write :

$$
\begin{equation*}
S_{\mathrm{g}, \mathrm{u}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right)=\frac{1}{k_{\mathbf{i}}^{2}} \delta\left(k_{\mathrm{f}}-k_{\mathbf{i}}\right) \sum_{l, m} \mathrm{e}^{2 i \delta_{l}^{\mathrm{g}, \mathrm{u}}} Y_{l}^{m *}\left(\hat{k}_{\mathrm{f}}\right) Y_{l}^{m}\left(\hat{k}_{\mathfrak{i}}\right) \tag{B.4}
\end{equation*}
$$

(the notation is the same as in [1]).
Now, using (B.2) and (B.3) with definitions (1.a) and (1.b), one obtains :

$$
\begin{equation*}
S_{\mathrm{g}, \mathrm{u}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathbf{i}}\right)=S_{\mathrm{d}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathbf{i}}\right) \pm S_{\mathrm{t}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathbf{i}}\right) . \tag{B.5}
\end{equation*}
$$

Therefore :

$$
\begin{equation*}
S_{\mathrm{d}, \mathrm{t}}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right)=\frac{1}{k_{\mathrm{i}}^{2}} \delta\left(k_{\mathrm{f}}-k_{\mathrm{i}}\right) \sum_{l, m} \frac{\mathrm{e}^{2 i \delta_{l}^{\mathrm{g}}} \pm \mathrm{e}^{2 i \delta_{l}^{\mathrm{u}}}}{2} Y_{l}^{m *}\left(\hat{k}_{\mathrm{f}}\right) Y_{l}^{m}\left(\hat{k}_{\mathrm{i}}\right) . \tag{B.6}
\end{equation*}
$$

From (8) and (19), we then obtain :

$$
\begin{equation*}
A_{\mathrm{t}}=1-A_{\mathrm{d}}=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathbf{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathbf{i}}^{\prime}\right) k_{\mathrm{i}}^{-2} \delta\left(k_{\mathrm{i}}-k_{\mathrm{i}}^{\prime}\right) \sum_{l, m} \sin ^{2}\left(\delta_{l}^{\mathrm{g}}-\delta_{l}^{u}\right) Y_{l}^{m *}\left(\hat{k}_{\mathbf{i}}^{\prime}\right) Y_{l}^{m}\left(\hat{k}_{\mathrm{i}}\right) \tag{B.7}
\end{equation*}
$$

and :

$$
\begin{align*}
\bar{C}_{I} & =\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \int \mathrm{d}^{3} k_{\mathrm{f}} k_{\mathrm{i}}^{-2} \delta\left(k_{\mathrm{i}}-k_{\mathrm{i}}^{\prime}\right)\left(-\frac{i}{2}\right) \sum_{l, m}(-1)^{l} \sin \left[2\left(\delta_{l}^{\mathrm{g}}-\delta_{l}^{u}\right)\right] Y_{l}^{m *}\left(\hat{k}_{\mathrm{i}}^{\prime}\right) Y_{l}^{m}\left(\hat{k}_{\mathrm{i}}\right) \\
& =i A_{\mathrm{exh}}^{I} \tag{B.8}
\end{align*}
$$

In this expression, the factor $(-1)^{l}$ arises from the fact that a nuclear identity interference term is involved (this factor has already been discussed for formula (A.8) of the appendix of [1]).

Let us now take the function $u(\mathbf{k})$ given in (A.11) [Appendix of the preceding article]. We then obtain :

$$
\begin{equation*}
\sigma_{\mathrm{met} \mathrm{exch}}=4 \pi^{2} L^{2} A_{\mathrm{t}} \tag{B.9}
\end{equation*}
$$

and :

$$
\begin{align*}
A_{\mathrm{t}} & =\frac{1}{4 \pi L^{2} k_{0}^{2}} \sum_{l}(2 l+1) \sin ^{2}\left(\delta_{l}^{\mathrm{g}}-\delta_{l}^{\mathrm{u}}\right)  \tag{B.10.a}\\
A_{\mathrm{exch}}^{I} & =-\frac{1}{2} \frac{1}{4 \pi L^{2} k_{0}^{2}} \sum_{l}(-1)^{l}(2 l+1) \sin \left[2\left(\delta_{l}^{\mathrm{g}}-\delta_{l}^{\mathrm{u}}\right)\right] \tag{B.10.b}
\end{align*}
$$

We can therefore write :

$$
\begin{equation*}
\sigma_{\mathrm{metexch}}=\pi k_{0}^{-2} \sum_{l}(2 l+1) \sin ^{2}\left(\delta_{l}^{\mathrm{g}}-\delta_{l}^{u}\right) \tag{B.11.a}
\end{equation*}
$$

and [cf. (26)] :

$$
\begin{equation*}
\kappa_{I}=-\frac{\pi}{2 k_{0}^{2} \sigma_{\mathrm{met} \operatorname{exch}}} \sum_{l}(-1)^{l}(2 l+1) \sin \left[2\left(\delta_{l}^{\mathrm{g}}-\delta_{l}^{\mathrm{u}}\right)\right] \tag{B.11.b}
\end{equation*}
$$

$\left\{\right.$ note that no $(-1)^{l}$ appears in the coefficient $\kappa$ of reference [7] \}. Here also, as in the case of spin exchange, one sees that $\sigma_{\text {metexch }}$ remains finite when $k_{0} \rightarrow 0$ (low energy limit), but that $\kappa_{I}$ diverges. Nuclear identity terms should therefore become dominant in very low temperature optical pumping experiments with ${ }^{3} \mathrm{He}$ or ${ }^{3} \mathrm{He}-{ }^{4} \mathrm{He}$ mixtures [28] (for example, the shift of the magnetic resonance line discussed in section 2.2 .2 should exceed the width of this line due to metastability exchange).

## APPENDIX II

In this Appendix II, we study in more detail how particle identity effects change the nuclear spin state of two colliding ${ }^{3} \mathrm{He}$ atoms, both in the ground state. We have seen that no such effect can be observed in optical pumping experiments where an integral is taken over all initial and final velocities of the atoms. Nevertheless, in atomic beam experiments, it is possible to study the atoms scattered in a particular direction. We shall then come back to equation (34), but without summing over all possible final scattering
directions $\hat{k}_{\mathrm{f}}$. This will lead us to distinguish between the spherical scattered wave and the transmitted wave, which depends on interference effects in the forward direction. At low collision energies, we shall see that the latter phenomenon is dominant and can be described by a effective nuclear spin hamiltonian. Although the scattering cross section (defined in terms of the external atomic variables) tends in general to a finite limit at vanishing collision energies, the cross section associated with the effective hamiltonian diverges.

Let us call $\Omega_{\mathrm{f}}$ the domain in the $\mathbf{k}_{\mathrm{f}}$ space which corresponds to the observed particles. We shall also denote as $-\Omega_{\mathrm{f}}$ the opposite domain obtained by reversing all $\mathbf{k}_{\mathbf{f}}$ values. Only an angular selection (no energy selection) of the particles is defined by $\Omega_{\mathrm{f}}$, and we call $\hat{\Omega}_{\mathrm{f}}$ and $-\hat{\Omega}_{\mathrm{f}}$ the corresponding domains for the angular variables $\hat{k}_{f}$ of the vector $\mathbf{k}_{\mathrm{f}}$. Equation (34) is then replaced by $\left({ }^{3}\right)$ :
$\left({ }^{3}\right)$ We assume here that the atoms studied are fermions. For bosons, a plus sign would replace the minus sign which stands in front of the terms in $\tilde{C}$ and $\tilde{C}^{*}$ in equation (C.1).

$$
\begin{equation*}
\tilde{\rho}\left(\Omega_{\mathrm{f}}\right)=\frac{1}{2} \tilde{A}\left(\Omega_{\mathrm{f}}\right) \rho_{1}+\frac{1}{2} \tilde{B}\left(\Omega_{\mathrm{f}}\right) \rho_{2}-\frac{1}{2}\left[\tilde{C}\left(\Omega_{\mathrm{f}}\right) \rho_{2} \rho_{1}+\tilde{C}^{*}\left(\Omega_{\mathrm{f}}\right) \rho_{1} \rho_{2}\right] \tag{C.1}
\end{equation*}
$$

with the notation :

$$
\begin{align*}
& \tilde{A}\left(\Omega_{\mathrm{f}}\right)=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \int_{\Omega_{\mathrm{f}}} \mathrm{~d}^{3} k_{\mathrm{f}} S\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S^{*}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right)  \tag{C.2.a}\\
& \tilde{B}\left(\Omega_{\mathrm{f}}\right)=\tilde{A}\left(-\Omega_{\mathrm{f}}\right)  \tag{C.2.b}\\
& \tilde{C}\left(\Omega_{\mathrm{f}}\right)=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \int_{\Omega_{\mathrm{f}}} \mathrm{~d}^{3} k_{\mathrm{f}} S\left(-\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) S^{*}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right) . \tag{C.2.c}
\end{align*}
$$

The terms in $\tilde{A}$ and $\tilde{B}$ have a simple physical interpretation. For distinguishable atoms, $\tilde{A}$ gives the probability for observing a scattering event where an atom, initially described by the wave packet $u\left(\mathbf{k}_{\mathbf{i}}\right)$, ends up with a linear momentum $\mathbf{k}_{\mathrm{f}}$ inside the domain $\Omega_{\mathrm{f}}$. The coefficient $\widetilde{B}$ gives the same probability, but for the atom which was initially described in the centre of mass frame by the wave packet $u\left(-\mathbf{k}_{\mathbf{i}}\right)$. The coefficient $\tilde{C}$ describes interference effects due to particle indistinguishability, and can be written :

$$
\begin{equation*}
\tilde{C}\left(\Omega_{\mathrm{f}}\right)=\tilde{X}\left(\Omega_{\mathrm{f}}\right)+i \tilde{Y}\left(\Omega_{\mathrm{f}}\right) \tag{C.3}
\end{equation*}
$$

where $\tilde{X}$ and $\tilde{Y}$ are real. The two last terms in the right hand side of (C.1) then become :

$$
\begin{equation*}
-\frac{1}{2} \tilde{X}\left(\Omega_{\mathrm{f}}\right)\left[\rho_{1}, \rho_{2}\right]_{+}+\frac{i}{2} \tilde{Y}\left(\Omega_{\mathrm{f}}\right)\left[\rho_{1}, \rho_{2}\right] \tag{C.4}
\end{equation*}
$$

The equations obtained are valid for any value of the nuclear spin. For spin $1 / 2$ nuclei, we have :

$$
\begin{equation*}
\rho_{\mathrm{i}}=\frac{1}{2}\left[1+\mathbf{P}_{i}, \sigma\right] \tag{C.5.a}
\end{equation*}
$$

$(i, j=1,2 ; \sigma$ is the operator with Pauli matrices as components) with :

$$
\begin{equation*}
0 \leqslant P_{i} \leqslant 1 \tag{C.5.b}
\end{equation*}
$$

Then :

$$
\begin{align*}
{\left[\rho_{1}, \rho_{2}\right]_{+} } & =\frac{1}{2}\left[1+\mathbf{P}_{1} \cdot \mathbf{P}_{2}+\left(\mathbf{P}_{i}+\mathbf{P}_{j}\right) \cdot \boldsymbol{\sigma}\right]  \tag{C.6.a}\\
& =\rho_{1}+\rho_{2}+\frac{1}{2}\left(\mathbf{P}_{1} \cdot \mathbf{P}_{2}-1\right)
\end{align*}
$$

$$
\begin{equation*}
\left[\rho_{1}, \rho_{2}\right]=\frac{i}{2} \sigma .\left(\mathbf{P}_{1} \times \mathbf{P}_{2}\right) \tag{C.6.b}
\end{equation*}
$$

For spin $1 / 2$ particles, the term in $\tilde{X}$ changes the trace of $\tilde{\rho}\left(\Omega_{\mathrm{f}}\right)$ by an amount proportional to $1+\mathbf{P}_{1} . \mathbf{P}_{2}$. Since $\mathbf{P}_{1} \cdot \mathbf{P}_{2}>-1$, this term decreases or increases the trace of $\tilde{\rho}\left(\Omega_{\mathrm{f}}\right)$, respectively when $\tilde{X}$ is positive or negative. In other words, the number of spins scattered in a given direction depends on particle identity effects, as is well known in collision theory (for example, if $\mathbf{P}_{1}=\mathbf{P}_{2}$, and $P_{1}=P_{2}=1$, no particle is scattered in a direction $\mathbf{k}_{\mathrm{f}}$ perpendicular to $\mathbf{k}_{\mathrm{i}}$ ).

The term in $\tilde{Y}$ gives a commutator, that is an effective nuclear spin hamiltonian acting on $\mathbf{I}_{1}$ and $\mathbf{I}_{2}$. We have already discussed such effects in detail in the case of metastability exchange. Also, a general discussion of how the spin states modulate interference effects can be given from (C.4) [see § 2.2.2 of reference [1] for a similar discussion].

Phase shift calculation. - Using the phase shift method, we can write :
$S\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathbf{i}}\right)=\frac{\delta\left(k_{\mathrm{f}}-k_{\mathbf{i}}\right)}{k_{\mathbf{i}}^{2}} \sum_{l, m} \mathrm{e}^{2 i \delta_{l}} Y_{l}^{m *}\left(\hat{k}_{\mathrm{f}}\right) Y_{l}^{m}\left(\hat{k}_{\mathbf{i}}\right)$
and obtain :

$$
\begin{align*}
\tilde{C}\left(\Omega_{\mathrm{f}}\right)=\int \mathrm{d}^{3} k_{\mathbf{i}} u\left(\mathbf{k}_{\mathbf{i}}\right) \int \mathrm{d}^{3} k_{\mathbf{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathbf{i}}^{\prime}\right) & {\left[k_{\mathbf{i}} k_{\mathbf{i}}^{\prime}\right]^{-1} \delta\left(k_{\mathbf{i}}-k_{\mathbf{i}}^{\prime}\right) \times } \\
& \times \sum_{l, m, l^{\prime}, m^{\prime}}(-1)^{l} \mathrm{e}^{2 i\left(\delta_{l}-\delta_{l}^{\prime}\right)} Y_{l}^{m}\left(\hat{k}_{\mathbf{i}}\right) Y_{l^{\prime}}^{m^{\prime}} *\left(\hat{k}_{\mathbf{i}}^{\prime}\right) \int_{\hat{\Omega}_{\mathrm{f}}} \mathrm{~d}^{2} \hat{k}_{\mathrm{f}} Y_{l}^{m *}\left(\hat{k}_{\mathrm{f}}\right) Y_{l^{\prime}}^{m^{\prime}}\left(\hat{k}_{\mathrm{f}}\right) \tag{C.8}
\end{align*}
$$

[the expression of $\tilde{A}\left(\Omega_{\mathrm{f}}\right)$ is simply obtained by suppressing the sign factor $(-1)^{l}$ in the summation]. If the domain $\Omega_{\mathrm{f}}$ is extended to all directions ( $4 \pi$ steradians), the integration over $\mathrm{d}^{2} \hat{k}_{\mathrm{f}}$ in (C.8) gives $\delta_{l l^{\prime}} \delta_{m m^{\prime}}$, so that the sum over $l$ and $m$ introduces a delta function $\left\langle\hat{k}_{\mathbf{i}} \mid-\hat{k}_{\mathbf{i}}^{\prime}\right\rangle$ peaked at opposite directions of $\hat{k}_{\mathrm{i}}$ and $\hat{k}_{\mathrm{i}}^{\prime}$. Since we assume that the product
$u\left(\mathbf{k}_{\mathbf{i}}\right) u\left(-\mathbf{k}_{\mathbf{i}}\right)$ is always zero, we find again that $\widetilde{C}(4 \pi)=C=0$, as already obtained in $\S 2.2 .2$. But, if $\Omega_{\mathrm{f}}$ is a smaller domain, this cancellation does not occur in general.
Also, if all the phase shifts $\delta_{l}$ vanish, we expect that $\tilde{C}\left(\Omega_{\mathrm{f}}\right)=0$. This can be checked on (C.8) because the sum over $l$ and $m$ then gives a delta function
$\left\langle\hat{k}_{\mathrm{i}} \mid-\hat{k}_{\mathrm{f}}\right\rangle$ peaked at $\hat{k}_{\mathrm{i}}=-\hat{k}_{\mathrm{f}}$, and the sum over $l^{\prime}$ and $m^{\prime}$ a delta function $\left\langle\mathbf{k}_{\mathbf{i}}^{\prime} \mid \mathbf{k}_{\mathrm{f}}\right\rangle$ peaked at $\hat{k}_{\mathrm{i}}^{\prime}=+\hat{k}_{\mathrm{f}}$, so that the integration over $\mathbf{k}_{\mathrm{i}}$ and $\mathbf{k}_{\mathrm{i}}^{\prime}$ gives zero.

In order to separate effects which occur in the spherical scattered wave from effects concerning the transmitted wave, we set :

$$
\begin{equation*}
S\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right)=S_{0}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right)+\bar{S}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) \tag{C.9}
\end{equation*}
$$

with :

$$
\begin{aligned}
S_{0}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) & =\delta\left(\mathbf{k}_{\mathrm{f}}-\mathbf{k}_{\mathbf{i}}\right) \\
\bar{S}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right) & =\frac{\delta\left(k_{\mathrm{f}}-k_{\mathrm{i}}\right)}{k_{\mathrm{i}}^{2}} \sum_{l, m}\left[\mathrm{e}^{2 i \delta_{l}}-1\right] Y_{l}^{m *}\left(\hat{k}_{\mathrm{f}}\right) Y_{l}^{m}\left(\hat{k}_{\mathbf{i}}\right) .
\end{aligned}
$$

All coefficients $\tilde{A}, \tilde{B}, \tilde{C}$ then appear as the sum of 4 terms, one bilinear in $S_{0}$, one bilinear in $\bar{S}$, and two crossed interference terms. The term bilinear in $\bar{S}$ concerns the spherical scattered wave, and the three others the transmitted wave.
Since we are interested here in particle identity effects, we shall only study the four contributions to $\tilde{C}$. Then, the first term, bilinear in $S_{0}$, actually vanishes, as can easily be shown by replacing in (C.2.c) both $S$ functions by $S_{0}$. We then have :

$$
\begin{equation*}
\tilde{C}\left(\Omega_{\mathrm{f}}\right)=\tilde{C}_{1}\left(\Omega_{\mathrm{f}}\right)+\tilde{C}_{2}\left(\Omega_{\mathrm{f}}\right)+\tilde{C}_{3}\left(\Omega_{\mathrm{f}}\right) \tag{C.11}
\end{equation*}
$$

with :

$$
\begin{align*}
& \tilde{C}_{1}\left(\Omega_{\mathrm{f}}\right)=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int_{\Omega_{\mathrm{f}}} \mathrm{~d}^{3} k_{\mathrm{f}} u^{*}\left(\mathbf{k}_{\mathrm{f}}\right) \bar{S}\left(-\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}\right)  \tag{C.12.a}\\
& \tilde{C}_{2}\left(\Omega_{\mathrm{f}}\right)=\int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right) \int_{\Omega_{\mathrm{f}}} \mathrm{~d}^{3} k_{\mathrm{f}} u\left(-\mathbf{k}_{\mathrm{f}}\right) \bar{S}^{*}\left(\mathbf{k}_{\mathrm{f}}, \mathbf{k}_{\mathrm{i}}^{\prime}\right) . \tag{C.12.b}
\end{align*}
$$

The number $C_{3}\left(\Omega_{\mathrm{f}}\right)$ is simply obtained by replacing in (C.2.c) $S$ by $\bar{S}$. We note that

$$
\begin{equation*}
\tilde{C}_{1}\left(\Omega_{\mathrm{f}}\right)=\tilde{C}_{2}^{*}\left(-\Omega_{\mathrm{f}}\right) . \tag{C.12.c}
\end{equation*}
$$

Particle identity effects in the spherical scattered wave. - If the domain $\Omega_{\mathrm{f}}$ is chosen so that $u\left(\mathbf{k}_{\mathrm{f}}\right)$ and $u\left(-\mathbf{k}_{\mathrm{f}}\right)$ are always zero inside this domain, the atoms which are studied are only scattered atoms. The numbers $\tilde{C}_{1}$ and $\tilde{C}_{2}$ are then zero according to equations (C.12), and therefore $C=\tilde{C}_{3}$ in this case. Expression (C.10) can be used to evaluate $\widetilde{C}_{3}$ and one obtains:

$$
\begin{align*}
& \tilde{C}_{3}\left(\Omega_{\mathrm{f}}\right)=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right)\left[k_{\mathrm{i}} k_{\mathrm{i}}^{\prime}\right]^{-1} \delta\left(k_{\mathrm{i}}-k_{\mathrm{i}}^{\prime}\right) \times \\
& \times \sum_{l, m, l^{\prime}, m^{\prime}}(-1)^{l}\left[\mathrm{e}^{2 i \delta_{l}}-1\right]\left[\mathrm{e}^{-2 i \delta_{l^{\prime}}}-1\right] Y_{l}^{m}\left(\hat{k}_{\mathrm{i}}\right) Y_{l^{\prime}}^{m *}\left(\hat{k}_{\mathrm{i}}^{\prime}\right) \tag{C.13}
\end{align*} \int_{\hat{\Omega}_{\mathrm{f}}} \mathrm{~d}^{2} \hat{k}_{\mathrm{f}} Y_{l}^{m *}\left(\hat{k}_{\mathrm{f}}\right) Y_{l^{\prime}}^{m^{\prime}}\left(\hat{k}_{\mathrm{f}}\right) .
$$

Here, the presence of two convergence factors [ $\left.\mathrm{e}^{2 i \delta_{l}}-1\right]$ and $\left[\mathrm{e}^{2 i \delta_{l}}-1\right]$ puts an upper limit on the values of $l$ and $l^{\prime}$ which significantly contribute to the sum [this was not the case in (C.8)]. We can now use the wave packet $u(\mathbf{k})$ given in (A.11) in the appendix of reference [1] and take the limit $\varepsilon \rightarrow 0, L \rightarrow \infty$, without convergence problems. We then obtain :

$$
\begin{equation*}
\tilde{C}_{3}\left(\Omega_{\mathrm{f}}\right)=\frac{1}{L^{2} k_{0}^{2}} \sum_{l, m, l, m^{\prime}}(-1)^{y}\left[\mathrm{e}^{2 i \delta_{l}}-1\right]\left[\mathrm{e}^{-2 i \delta_{r_{r}}}-1\right] \times Y_{l}^{m}\left(\hat{k}_{0}\right) Y_{l^{\prime}}^{m * *}\left(\hat{k}_{0}\right) \int_{\Omega_{\mathrm{f}}} \mathrm{~d}^{2} \hat{k}_{\mathrm{f}} Y_{l}^{m *}\left(\hat{k}_{\mathrm{f}}\right) Y_{l^{\prime}}^{m^{\prime}}\left(\hat{k}_{\mathrm{f}}\right) . \tag{C.14}
\end{equation*}
$$

The real part and imaginary part of (C.14) give the anticommutator and effective hamiltonian terms in the spin density operator evolution.

One can also assume that the observation domain $\Omega_{\mathrm{f}}$ is extended to $4 \pi$ steradians. The integration over $\mathrm{d}^{2} \hat{k}_{\mathrm{f}}$ in (C.13) then gives $\delta_{l \prime} \delta_{m m^{\prime}}$ and $C_{3}$ takes on the value :

$$
\begin{equation*}
\tilde{C}_{3}(4 \pi)=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right)\left[k_{\mathrm{i}} k_{\mathrm{i}}^{\prime}\right]^{-1} \delta\left(k_{\mathrm{i}}-k_{\mathrm{i}}^{\prime}\right) \times \sum_{l, m}(-1)^{l} 4 \sin ^{2} \delta_{l} Y_{l}^{m}\left(\hat{k}_{\mathrm{i}}\right) Y_{l}^{m *}\left(\hat{k}_{\mathrm{i}}^{\prime}\right) \tag{C.15.a}
\end{equation*}
$$

or :

$$
\begin{equation*}
\tilde{C}_{3}(4 \pi)=\frac{1}{4 \pi L^{2} k_{0}^{2}} \sum_{l}(-1)^{y}(2 l+1) 4 \sin ^{2} \delta_{l} \tag{C.15.b}
\end{equation*}
$$

$\tilde{C}_{3}(4 \pi)$ is therefore a real coefficient in this case [the effective hamiltonian term then disappears in (C.4)]. Since the summation over $l$ corresponds to an alternating series, $\tilde{C}_{3}$ is likely to have larger values at low energies, when only a few phase shifts have significant values.

A cross section for change of the spin state of the scattered atoms can be defined by [see Ref. [1], equation (A.19)] :

$$
\begin{align*}
\tilde{\sigma}_{3} & =4 \pi^{2} L^{2} C_{3}(4 \pi) \\
& =\frac{\pi}{k_{0}^{2}} \sum_{l}(-1)^{l}(2 l+1) 4 \sin ^{2} \delta_{l} . \tag{C.16}
\end{align*}
$$

At low collision energies, only $l=0$ contributes to this sum, and when $k_{0} \rightarrow 0, \tilde{\sigma}_{3}$ tends to a finite value $\left({ }^{4}\right)$.
Particle identity effects in the transmitted wave. - If $\hat{\Omega}_{\mathrm{f}}$ is a very small angular domain, formula (C.14) shows that $\widetilde{C}_{3}$ can be neglected. On the other hand, if $\Omega_{\mathrm{f}}$ contains all $\mathbf{k}_{\mathrm{f}}$ values where $u\left(\mathbf{k}_{\mathrm{f}}\right)$ is not zero, the coefficient $\tilde{C}_{1}$ can be obtained by extending in (C.12.a) the integral over $\mathbf{k}_{\mathrm{f}}$ to all space. Nevertheless, if we assume that $u\left(\mathbf{k}_{\mathrm{f}}\right)$ is always zero inside the domain $-\Omega_{\mathrm{f}}$, formula (C.12.b) shows that $\widetilde{C}_{2}$ vanishes. The coefficient $\widetilde{C}$ is then given by :

$$
\begin{align*}
\tilde{C}(\text { forward }) & =\tilde{C}_{1}(4 \pi)=\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathbf{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathbf{i}}^{\prime}\right) \bar{S}\left(-\mathbf{k}_{\mathrm{i}}^{\prime}, \mathbf{k}_{\mathrm{i}}\right) \\
& =\int \mathrm{d}^{3} k_{\mathrm{i}} u\left(\mathbf{k}_{\mathrm{i}}\right) \int \mathrm{d}^{3} k_{\mathrm{i}}^{\prime} u^{*}\left(\mathbf{k}_{\mathrm{i}}^{\prime}\right)\left[k_{\mathrm{i}} k_{\mathrm{i}}^{\prime}\right]^{-1} \delta\left(k_{\mathbf{i}}-k_{\mathrm{i}}^{\prime}\right) \sum_{l, m}(-1)^{l}\left[\mathrm{e}^{2 i \delta_{l}}-1\right] Y_{l}^{m}\left(\hat{k}_{\mathrm{i}}\right) Y_{l}^{m *}\left(\hat{k}_{\mathbf{i}}^{\prime}\right) \tag{C.17}
\end{align*}
$$

If $u\left(\mathbf{k}_{\mathrm{i}}\right)$ is given by formula (A.11) of reference [1], we obtain :

$$
\begin{align*}
& \tilde{C}(\text { forward })= \\
& \quad=\frac{1}{4 \pi L^{2} k_{0}^{2}} \sum_{l}(-1)^{l}(2 l+1)\left[\mathrm{e}^{2 i \delta_{l}}-1\right] . \tag{C.18}
\end{align*}
$$

Since :

$$
\begin{equation*}
\mathrm{e}^{2 i \delta_{l}}-1=-2 \sin ^{2} \delta_{l}+i \sin 2 \delta_{l} \tag{C.19}
\end{equation*}
$$

$\tilde{C}$ has in this case a real and an imaginary part, giving rise to a commutator and an anticommutator in (C.4)

Here also, $\tilde{C}$ is given by an alternating series and is likely to have negligible values at high energies, when many values of $l$ have an important phase shift. At lower energies, when $\tilde{C}$ is not negligible, the particle identity effects change the spin density operator of the forward scattered atoms (transmitted beam) according to (C.4) and (C.18).

We can define two quantities :

$$
\begin{align*}
& \tilde{\sigma}_{I}=4 \pi^{2} L^{2}|\tilde{X}| \text { (forward) } \\
& \tilde{\sigma}_{I}^{\prime}=4 \pi^{2} L^{2}|\tilde{Y}| \text { (forward) } \tag{C.20}
\end{align*}
$$

The latter for example could be called a cross section for nuclear spin rotation ( ${ }^{5}$ ) and describes nuclear identity effects in the transmitted beam. At vanishing collision energies, $\tilde{\sigma}_{I}$ tends to a finite value, but $\tilde{\sigma}_{I}^{\prime}$

[^3]diverges. The situation is reminiscent of the divergence of $\kappa$ and $\kappa^{\prime}$ discussed in the Appendix of reference [1].

## Remarks :

(i) If $\hat{\Omega}_{\mathrm{f}}$ is changed into $-\hat{\Omega}_{\mathrm{f}}, \tilde{C}_{1}$ vanishes but $\tilde{C}_{2}$ does not. It is actually simple to show that $\tilde{C}_{2}$ is given by the complex conjugate of expressions (C.17) and (C. 18).

Changing $\hat{\Omega}_{\mathrm{f}}$ into $-\hat{\Omega}_{\mathrm{f}}$ amounts to studying the atoms in the target after interaction, instead of the particles in the transmitted beam. We see that this operation reverses the sign of the effective hamiltonian (propertional to $C_{I}$ ) acting on the nuclear spins. This is physically satisfying since the total spin momentum of the atoms is conserved during the interaction. On the other hand, the anticommutators terms in (C.4) remain the same.

If now the domain $\Omega_{\mathrm{f}}$ is extended to $4 \pi$ steradians in equations (C.12), $\tilde{C}_{1}$ and $\tilde{C}_{2}$ both differ from zero and are complex conjugate. It is then easy to show from (C.15.b), (C.18) and (C.19) that, in this case :
$\tilde{C}(4 \pi)=\tilde{C_{1}}(4 \pi)+\tilde{C}_{2}(4 \pi)+\widetilde{C_{3}}(4 \pi)=0$.
The nuclear identity effects therefore disappear if all atoms (scattered, transmitted, target) are taken into account. This was predictable since no real nuclear spin hamiltonian exists in the process which has been studied.
(ii) The divergence of $\tilde{\sigma}_{I}^{\prime}$ is related to the phase of the wave scattered in the forward direction. The scattering amplitude is given by :

$$
f_{k}(\theta)=\frac{1}{k} \sum_{l=0}^{\infty} \sqrt{4 \pi(2 l+1)} \mathrm{e}^{\mathrm{i} \delta_{l}} \sin \delta_{l} Y_{l}^{0}(\theta)
$$

When the collision energy vanishes, the real part of
$f_{k}(\theta)$ tends to a finite value but its imaginary part is first order in $k_{0}$. Then, according to the optical theorem

$$
\sigma_{\mathrm{tot}}=\frac{4 \pi}{k_{0}} \operatorname{Im}\left\{f_{k}(\theta=0)\right\}
$$

remains finite if $k_{0} \rightarrow 0$, but this is true only because
$\sigma_{\text {tot }}$ does not depend on the real part of the forward scattering amplitude, which is much larger than the imaginary part at low energies. On the other hand, the modification of the spin states due to particle identity depends on this real part, which is why particle identity effects then become dominant.

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[^1]:    $\left({ }^{1}\right)$ If the two atoms belong to two different isotopes, we ignore any difference between the excitation energies of the two metastable levels (nuclear mass or volume effect, etc...). This assumption is not essential and is made only for the sake of simplicity. As in the study of spin exchange collisions, we also neglect any effect of the hyperfine coupling during the metastability exchange process. At very low collision energies (low temperature experiments) both these approximations would no longer be valid.

[^2]:    $\left(^{2}\right)$ Since $J>I, \mathbf{F}$ and $\mathbf{I}$ are antiparallel inside the $F=1 / 2$ sublevel (and of course parallel inside the $F=3 / 2$ sublevel).

[^3]:    ( ${ }^{4}$ ) Similarly, equation (C.14) allows one to study low energy scattering in a particular direction. This equation shows that, when $k_{0} \rightarrow 0$, the real part of $C_{3}\left(\Omega_{\mathrm{f}}\right)$ tends to a finite value, but the imaginary part (effective hamiltonian) to zero.
    ${ }^{5}$ ) Since we do not study scattered particles here but changes of the spin state of the transmitted particles, this is an extension of the usual definition for a cross section.

