Collisional excitation transfer in high magnetic fields. I. Theory

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The effects of strong magnetic fields on thermal collisions in a vapor are reviewed. Semiclassical and quantum-mechanical symmetry properties of the relaxation matrix are established for resonant collisions between identical atoms and nonresonant collisions with a structureless partner. The variations with field strength of the transfer rates between Zeeman sublevels for R^{-3} dipole-dipole interaction and R^{-6} Van der Waals interaction are obtained with an exact semiclassical computation of the collision matrix. These are then compared with those predicted with an approximate formulation by means of the symmetrical correlation function for the potential.

I. INTRODUCTION

Strong magnetic fields are of particular interest to the study of weakly inelastic collisions in a vapor as they offer a very simple means for continuously varying the energy difference between the Zeeman substates of an atom over a considerable energy range (of about $\frac{1}{10}kT$ currently obtained with steady fields). The effects of a magnetic field on the collisional process in a vapor are twofold. The parameters describing the relaxation are field dependant. Secondly, the lack of invariance in the system under time reversal and spatial rotation produces a breakdown of the statistical rotational invariance generally satisfied in zero external fields. These effects are important when the energy difference between levels is about $\hbar(\tau_c)^{-1}$, where τ_c is the mean duration[1] of the collision or the correlation time of the potential.

In the following sections, we will investigate the symmetry properties of the relaxation matrix in various physical situations in the presence of strong magnetic fields using first a semiclassical and then a quantum-mechanical derivation with detailed balance.

Predictions obtained by means of an approximate theory based on the symmetrical correlation function of the potential will then be compared with exact numerical results for $J = 1 \rightarrow J = 0$ resonance transitions and for various kinds of potentials.

Several experimental investigations of collisional excitation transfer between Zeeman sublevels in strong magnetic fields have been performed on Hg and Na vapors and will be reported in forthcoming papers. They reveal the possibility of direct measurement of various collision parameters such as correlation time and correlation function, anisotropy of the potential, and also selection rules during the collision process.

II. SYMMETRIES OF THE RELAXATION PROCESS

A. Symmetry considerations

The relaxation process in a vapor is in general statistically isotropic provided the system is not subjected to external fields.[2,3] In fact this conclusion requires the fulfillment of additional conditions, e.g., broad line excitation and isotropic velocity distribution of the atoms. Then the relaxation matrix $\langle \mathfrak{M} \rangle$, which conveniently describes the process, is a scalar in Liouville space. The relaxation rates, which are matrix elements of $\langle \mathfrak{M} \rangle$ satisfy (in an irreducible tensorial basis)

$$\langle\langle kq | \langle \mathfrak{M} \rangle | k'q' \rangle\rangle = \delta_{kk'} \, \delta_{qq'} g^k , \tag{1}$$

where g^k is the relaxation rate of the (kq) component of the density matrix. Of course, notations in (1) omit many dummy indices, referring to the fact that there is usually more than one rank-k tensor operator subtending Liouville space. We will use this convention in the following to simplify notation.

When a vapor is submitted to an external magnetic field, while all other conditions remain valid relation (1) no longer holds since the requirement of isotropy of the system is not fulfilled.[4] Moreover, the system no longer possesses time-reversal invariance. Statistical symmetries still exist, and result from rotational invariance around the field direction, invariance in parity operation, and also from invariance in the *product* of reflections in planes containing the field direction and time-reversal operation. This last operation, which looks like a dynamical symmetry for the system, results from intuitive arguments that the field is reversed in each

operation, and that their product consequently leaves the field unchanged. These are basically the main points developed in the following subsections. At first examination, it seems more convenient to seek these new symmetry properties in a dyadic Zeeman basis (in the direction of the field), but in fact the use of a tensorial irreducible basis built on Zeeman's is still of great interest.

As concerns the relaxation matrix for the whole system with zero external field, the time-reversal operation does not produce any additional relations between relaxation coefficients[5] when they satisfy the isotropy condition (1). But the use of time-reversal invariance with some additional transformation[6] to calculate the result of one definite collisional process (within, for example, the framework of impact approximation) leads to considerable simplification of the computational procedure.[7]

One must also remark that as the system in a strong field is not invariant under the time-reversal operation, the usual proof of detailed balance which supposes the validity of this property[8] breaks down.

B. Establishing symmetries

Statistical symmetry properties of the relaxation process in strong magnetic fields may be established in two different ways. There is a purely quantum-mechanical treatment which is the only correct way of satisfying the laws of conservation of quantum momentum and energy in the external field. Secondly, there is a semiclassical treatment of the collision process in the framework of the impact-parameter approximation.

In the simple case where there is no external field, significant difficulties[6] arise in the latter method from the partition between internal and external (nucleus positions) orbital variables and from the t parametrization of the positions. This method permits the conservation of neither energy nor angular momentum during each collision process, and the expression of time-reversal invariance depends strongly upon the choice of basis.[9] Nevertheless, this is in general of little importance for the final results when the conditions of applicability of the impact-parameter approximation are fulfilled.

For the present problem the nonzero Zeeman splitting ΔE of the levels allow weakly inelastic transitions to occur during the collision. A one-trajectory impact-parameter treatment obviously violates energy- and angular-momentum-conservation laws. Therefore the treatment of inter-Zeeman transitions will be significant only for $\Delta E \ll kT$ and for large mean values of the mo-

mentum of the partial waves, i.e., essentially for collisions between heavy atoms with long-range interactions.

Having recalled these well-known difficulties arising from the use of the impact-parameter approximation, it is not surprising that with this method one obtains symmetry properties that are only limiting cases of the true ones obtained with a quantum-mechanical derivation and which are only valid in the weak-field limit ($\Delta E \ll kT$).

C. Semiclassical derivation of symmetry properties

1. Hypothesis of derivation

We suppose that the interaction potential is invariant under time reversal and in plane reflections around the internuclear axis.[6] Such potentials are, for example, dipole-dipole interaction between identical atoms and long-range Van der Waals anisotropic interaction between an excited atom A and a structureless spherically symmetric partner X. More generally, this treatment concerns all electrostatic potentials which possess these symmetries.

Moreover, we suppose for simplification that the trajectory of the atoms is rectilinear and of constant velocity; the results remain valid with the proper classical trajectory, provided the impact-parameter direction $\vec{b}$ is an axis of symmetry.

A frame (xyz) with x and y axes parallel to the impact parameter $\vec{b}$ and relative velocity $\vec{v}$, respectively, will be associated with a given collision process in space. This frame is derived from the fixed frame in space (with the Z axis parallel to the magnetic field $\vec{B}$) by the rotation $\mathfrak{R}^{-1}(\varphi, \theta, \gamma)$, where $(\varphi\theta\gamma)$ is Euler's angle (following the definition of Messiah).[8]

The general form of the interaction potential in the fixed frame is then[10-12]

$$V = qf(R) \sum_{q_1} (-)^{q_1} U^2_{-q_1} T^2_{q_1} \propto (U^{(2)} \otimes T^{(2)})^{(0)} ,$$

with   (2)

$$U^{(2)} = (u^{(1)} \otimes u^{(1)})^{(2)} ,$$

and $u^{(1)}$ the unit vector along the internuclear axis. In (2), we neglect the isotropic part in the internal variables (which is nonzero, e.g., for Van der Waals interaction), q is the strength of the interaction,[11,12] and $f(R)$ its R dependence. A rank-2 tensor on the internal coordinates and on the orbital variables ($U^{(2)}$), V is a scalar for the whole system. The $\{U^2_q\}$ depend on $(\varphi\theta\gamma)$ and on $x = vt/b$, which in reduced variables results from the t parametrization of the potential. The $\{U^2_q\}$ have simple expressions in the (xyz) col-

lision frame[13] which are readily obtained from

$$U_{q_1}^2(\varphi, \theta, \gamma, x) = \sum_{q_2} u_{q_2}^2(x) R_{q_2 q_1}^{(2)}(\varphi \theta \gamma) . \qquad (3)$$

Explicit expressions are given in Appendix I.

As the interaction is of purely orbital nature (exchange interaction is excluded), $T^{(2)}$ is a rank-2 tensor built on the orbital angular momentum $\vec{L}$ for A^*-X collisions, and on the electric dipole moments $P_{(1)}^{(1)}$ and $P_{(2)}^{(1)}$ of the atoms for A^*-A resonant collisions. It follows then that

$$^{11}T^{(2)} = (P_{(1)}^{(1)} \otimes P_{(2)}^{(1)})^{(2)} . \qquad (4)$$

2. Relations between semiclassical collision matrices

The analysis is done for A^*-A collisions ($J = 1 \rightarrow J = 0$ transitions) and A^*-X collisions ($J = 1$ excited state).

The evolution during the collision process is due to the interaction potential and the Zeeman Hamiltonian (assuming no LS decoupling effects). In the interaction picture, Schrödinger's equation is

$$i \frac{d}{dx} |\psi(x)\rangle = P(\varphi, \theta, \gamma, x) |\psi(x)\rangle , \qquad (5)$$

with

$$P(\varphi, \theta, \gamma, x) = e^{i \eta^J B^x} V(x) e^{-i \eta^J B^x}$$
$$= q f(R) \sum_{q_1} (-)^{q_1} U_{-q_1}^2 e^{i \eta_q {}^1 x} T_{q_1}^{(2)} . \qquad (6)$$

$\Sigma(\varphi \theta \gamma)$ is the collision matrix associated with (5). To solve the relaxation problem one thus needs to know $\Sigma(\varphi \theta \gamma)$ for each orientation of the collision plane relative to the field.

In the case of A^*-A collisions, (5) is invariant under the exchange of atoms. Then the symmetric and antisymmetric states evolve independently in their respective $+P$ and $-P$ potentials. In that sense, a complete formal analogy exists between A^*-X and A^*-A collisions for $J = 1 \rightarrow J = 0$ transitions.[12]

The basic idea of the investigations of symmetry properties is to search for relations between collision matrices (in the fixed frame) for *different collision processes in space*. These relations are established[11] and interpreted in the Appendix and used in Sec. II C 3.

3. Symmetry of the relaxation process

The semiclassical relaxation matrix is defined following usual conventions such that[14] $\langle \mathfrak{M} \rangle$ is given by

$$\langle \mathfrak{M} \rangle \rho = \int \int f(v) v^2 \, dv \, b \, db \langle \Sigma_i \rho \Sigma_i^\dagger (\varphi \theta \gamma) \rangle - \rho \delta_{11} , \qquad (7)$$

ρ being the density matrix, and $f(v)$ the (isotropic) velocity distribution. The brackets indicate angular average over the angles of $\vec{b}$ and $\vec{v}$. It is more convenient to characterize $\langle \mathfrak{M} \rangle$ by means of its matrix elements in a $\{T_q^k\}$ or standard $\{|JM\rangle\langle J'M'|\}$ basis, giving

$$g^{\alpha \alpha'} = \langle\!\langle \alpha | \langle \mathfrak{M} \rangle | \alpha' \rangle\!\rangle . \qquad (8)$$

a. Symmetries for A^*-X collisions. The principle of the deduction is to use Eqs. (A1)–(A5) in taking the angular averages in (7) and (8). This gives after a little algebra the following sets of relations:

$$g_{qq'}^{kk'} = \delta_{qq'} g_q^{kk'} , \quad g^{(rr')(pp')} = \delta_{r-r', p-p'} g^{(rr')(pp')} , \qquad (9a)$$

$$g_q^{kk'} = g_q^{k'k} , \quad g^{(rr')(pp')} = g^{(pp')(rr')} , \qquad (9b)$$

$$g_q^{kk'} = g_{-q}^{kk'*} , \quad g^{(rr')(pp')} = g^{(r'r)(p'p)*} , \qquad (9c)$$

$$g_q^{kk'}(+) = (-)^{k+k'} g_q^{kk'}(-) ,$$
$$g^{(rr')(pp')}(+) = g^{(-r-r')(-p-p')*}(-) , \qquad (9d)$$

$$g_0^{0k} = g_0^{k0} = 0 , \quad \sum_p g^{(rr)(pp)} = 0 . \qquad (9e)$$

Some relations may also be deduced for the shift and broadening of the optical lines.[12]

Relations (9) can be interpreted as follows.

(9a) is the expression for rotational invariance around the field.

(9b) expresses the invariance in the *product* of time-reversal operation and XOZ-plane reflections.[15]

(9c) is a general relation[16] due to the Hermiticity of the density matrix.

(9d) is not the expression of a symmetry property, but permits one to relate the parameters of relaxation in the two cases in which the relative positions of the Σ and Π potential-energy curves of the system are inverted. The existence of this relation is closely related to the particular form adopted in (2) for the anisotropic part of the potential, which permits one to interpret $(-V)$ as the potential for another physical situation.[12] Also note that the derivation of this relation in the framework of impact-parameter theory with straight-line trajectories supposes that the isotropic part of the potential is not used *for trajectory calculations*. If it is used the very simple situation which obtains here (where the relaxation depends only upon the anisotropic part of the potential) will no longer be correct, and (9d) breaks down. Of course, in a fully quantum-mechanical treatment such an approximation does not apply, as the effect of the potential on the wave function would be included.

(9e) expresses the conservation of population during the collision process and comes from the

unitarity of Σ matrices. This supposes that the perturber X is structureless and cannot be strongly perturbed during the collision process.

b. Symmetries for $A*$-A collisions. A natural partition of the system between two classes corresponding to the initially excited atoms (class 1) and ground-state atoms (class 2) is generally made.[14] One always supposes that the density of excited atoms is small compared to that of ground-state atoms, excluding e.g. spin-exchange collisions and collisions in a saturating laser field.

As remarked above, Schrödinger's equation is invariant under the exchange of atoms. The evolution of the system is then equivalent to that of the symmetric states in the potential $+V$ with the associated $\Sigma(+)$ collision matrix and of the antisymmetric states in the potential $-V$ with the $\Sigma(-)$ collision matrix. The evolution of each subset is equivalent to that obtained in $A*$-X collisions. Then the relations of Appendix I are verified by $\Sigma(+)$. But now, the collision matrices for each class of atoms are given by

$$\Sigma_{\frac{1}{2}} = \tfrac{1}{2}[\Sigma(+) \pm \Sigma(-)], \qquad (10)$$

where $\Sigma_{\frac{1}{2}}$ are not unitary matrices. From the definition (8) and relations (A1)–(A5) one then deduces the following set of relations for each class i of atoms:

$$g_{qq'}^{kk'}(i) = \delta_{qq'} g_q^{kk'}(i),$$
$$g^{(rr')(pp')}(i) = \delta_{r-r',\,p-p'} g^{(rr')(pp')}, \qquad (11a)$$

$$g_q^{kk'}(i) = g_q^{k'k}(i), \qquad g^{(rr')(pp')}(i) = g^{(pp')(rr')}(i), \qquad (11b)$$

$$g_q^{kk'}(i) = g_{-q}^{kk'}(i)*, \qquad g^{(rr')(pp')}(i) = g^{(r'r)(p'p)*}(i), \qquad (11c)$$

$$g_q^{kk'}(i) = (-)^{k+k'} g_q^{kk'}(i),$$
$$g^{(rr')(pp')}(i) = g^{(-r-r')(-p-p')*}. \qquad (11d)$$

The interpretation of relations (11) is that developed in Sec. II C 3b [Eqs. (9)]. But there is no equivalence of conservation laws, as $\Sigma_{\frac{1}{2}}$ are not unitary transformations. Not identical to (9d), (11d) is now a new symmetry property for the system. Concerning the difference from the situation in Sec. II C 3 a, the solutions of Schrödinger's equation in the $+V$ (symmetric states) and $-V$ (antisymmetric states) potentials are simultaneously involved in the solution of the physical problem for identical atoms as expressed in Eq. (10). All remarks made on the validity of (9d) remain valid, except that in true physical situations the isotropic part of the potential is now much weaker than R^{-3} dipole-dipole interaction (main anisotropic part), and the various assumptions (straight-line trajectories and impact approximation) are in general well verified.[17,18]

So although (11d) has no quantum-mechanical analog, it will probably be well verified with a quantum-mechanical treatment of the problem for not-too-strong magnetic fields ($\Delta E \ll kT$).

The collision matrix for the whole ensemble of atoms is defined through the action on each class separately[14] by

$$g(1+2) = g(1) + g(2), \qquad (12)$$

thus neglecting the correlation terms [crossed $\Sigma(+) \cdot \Sigma(-)$ terms]. This is of no practical importance since quantum-mechanical indistinguishability effects are negligible (for long-range interactions). Moreover, correlations do not have any physical meaning in our model, where atoms are far from each other before and after collision.

The coefficients $g(1+2)$ satisfy relations (11) and one additional relation,

$$g_0^{0k}(1+2) = g_0^{k0}(1+2) = 0, \qquad (13)$$

which expresses the conservation of population for the whole system.

The broadening and shift of the optical lines are only connected to the $\Sigma(+)$ collision matrix for the symmetric states[11]; this is a well-known result in super-radiance theory when one neglects retardation effects.[19]

These various relations show that the relaxation in high magnetic fields is strongly anisotropic. Some of the relations (9) take a form very similar to those obtained when the system is submitted to an external electric field,[15,16] the differences coming from the rather different behaviors of $\vec{E}$ and $\vec{B}$ under parity, plane reflections, and the time-reversal operation.[8]

D. Generalization for $A*$-X collisions

Relations (9) can be generalized following the methods of the Appendix to various situations, including the case of several fine-structure levels. In the case of a purely orbital interaction potential, (2) may be written in the form

$$V = q f(R) \sum_{JJ'} \sum_{q_1} b(LSJJ')(-)^{q_1} U_{-q_1}^{2\ JJ'} T_{q_1}^{(2)}, \qquad (14)$$

the $\{b\}$ being proportional only to the reduced matrix elements of the various operators and satisfying $b = b*$.

In the general case, the unperturbed Hamiltonian of the system is

$$H_0 = A\vec{L} \cdot \vec{S} + \mu_B \vec{B} \cdot (\vec{L} + 2\vec{S}). \qquad (15)$$

Several situations must be considered according to the relative orders of magnitude of the LS structure, magnetic interaction, and interaction

potential.[20] We always suppose that the various energy differences are small compared to kT.

1. Strong $\vec{L} \cdot \vec{S}$ coupling

If $A\vec{L} \cdot \vec{S} \gg H_{magn} \sim \tau_c^{-1}$ one can consider each fine-structure level separately in the interaction potential (14). Equations (9) are valid provided the proper phase factors $\epsilon = \pm 1$ are included, and hold exactly for population transfer.

If $H_{magn} \sim A\vec{L} \cdot \vec{S} \gg \tau_c^{-1}$, a partial decoupling of L and S due to the field occurs. The eigenvectors of (15) are then

$$|\tilde{J}M\rangle = \sum_{J'} d(LSJ')|J'M\rangle . \tag{16}$$

Transitions which are usually weak (as $\tau_c^{-1} \ll H_0$) may occur via the mixing of fine-structure sublevels.[5,20] Since H_0 does not depend linearly on M and the energy differences between the states $(\tilde{J}M)(\tilde{J}M')$ and $(\tilde{J}-M)$, $(\tilde{J}-M')$ are not the same, (9d) is not valid. The other relations (9) are valid in the basis of eigenvectors $|\tilde{J}M\rangle$.

2. Paschen-Back regime

If $\tau_c^{-1} \sim H_{magn} \gg A\vec{L} \cdot \vec{S}$, the problem is simplified by the purely orbital nature of the interaction potential. During the collision process which essentially perturbs $\vec{L}$, $\vec{S}$ is precessing around B. Then symmetry properties (9) hold for M_L, and $M_S = M_S'$.

3. Intermediate regime $A\vec{L} \cdot \vec{S} \sim H_{MAGN} \sim \tau_c^{-1}$

There is inter- and intramultiplet transfer by collision. If decoupling effects are still weak, the Zeeman approximation of (15) is valid and the derivation of Sec. II C may be used. Relations (9) are valid in J, but also hold for $J' \neq J$ (intermultiplet transitions) with convenient phase factors.

If decoupling effects are not negligible, (9d) does not hold as in Sec. II D 1. Between the eigenvectors $|\tilde{J}M\rangle$ of H_0 (9a) and (9b) are still valid, giving

$$g^{(\tilde{J}M\tilde{J}M)(\tilde{J}'M'\tilde{J}'M')} = g^{(\tilde{J}'M'\tilde{J}'M')(\tilde{J}M\tilde{J}M)} , \tag{17}$$

the demonstration of which needs some modification in the algebra of Appendix I, as the transformations of $|\tilde{J}M\rangle$ in $T(\xi)$ are not those of $|JM\rangle$.[8,21]

Of course, these conclusions are valid for long-range interaction. Practical physical situations are in general intermediate cases of the preceding, as the situation may change drastically with the values of b, v, and t, and thus requiring a more accurate analysis using, e.g., Hund's coupling schemes for each collision process.[22,23]

E. Generalization for $A^* A$ collisions

We consider the case of identical atoms possessing a structure both in the ground (j) and in the (J) excited states. We suppose the validity of the Zeeman approximation for the magnetic Hamiltonian. Some of the relations we derive are not valid if one includes the decoupling of LS structure due to the field.

1. Expressions of dipole-dipole interaction

Dipole-dipole interaction is still of the general form of (2), where the operator $^{11}T^{(2)}$ is given by (4) and corresponds to the $\{(j_1 j_1^+)1, (J_2 j_2^+)1; 2q\}$ coupling scheme.[24] The alternative coupling scheme is $\{(j_1, J_2)F_1; (J_1, j_2)F_2\}^+; 2Q\}$ and corresponds to $^{F_1 F_2}T^2$ operators constructed by successive coupling of the angular momentum of the two atoms, in the initial and final states. One then obtains a unified-atom description of the problem, making clear the analogy between A^*-A and A^*-X collisions. The two bases are related by a unitary transformation[8,25] with real coefficients.

a. Remarks. The second coupling scheme is of interest for expressing symmetry properties in zero field. The expression of rotational invariance is straightforward, since one is dealing with one unified atom system, so that the results for A^*-X collisions may immediately be transposed.[24] The first coupling scheme is useful for describing the perturbation of each class of atoms, since a partial trace is readily obtained in this representation.[24]

For a $J = 1 \rightarrow j = 0$ transition, the two bases coincide exactly, and so have convenient properties both for expressing symmetries and for dividing the system between each class of atoms. The problem is almost equivalent to that of collisions with a structureless partner, since the ground state of the atoms is spherically symmetric.

2. Zeeman Hamiltonian

The Landé factors of the excited and ground states are g_e and g_f, respectively, and

$$H_Z = \mu_B B\left[g_e(J)J_z + g_f(j)j_z\right] . \tag{18}$$

In the $|JM, jm\rangle$ uncoupled basis H_Z is diagonal, but not in the $|(Jj)Fm\rangle$ coupled one unless $g_e = g_f$.

3. Exchange of atoms

The interaction potential (2) is invariant under the exchange of atoms. The symmetric and antisymmetric states under exchange, which are just

$$|\pm JM, jm\rangle = 2^{-1/2}\left[|JM, jm\rangle \pm |jm, JM\rangle\right] , \tag{19}$$

evolve independently in the $+V$ and $-V$ potentials, respectively.

4. Derivation of symmetries

a. Special case of $g_e = g_f$. Invariant under the exchange of atoms, H_Z is diagonal in the coupled $|\pm, F M_F\rangle$ symmetrized basis. The problem is thus completely equivalent to that of collisions with a structureless partner, and so Eqs. (9) are valid in the $|\pm F M_F\rangle$ basis. The derivation of the relations in the uncoupled basis is straightforward, but the situation is of little physical interest.

b. Weak fine structure in ground and excited states $(A\tau_c \ll \hbar)$. The Zeeman Hamiltonian is then

$$H_Z = \mu_B \vec{B} \cdot (\vec{L} + \vec{l}) + 2\mu_B \vec{B} \cdot (\vec{S} + \vec{s}) . \tag{20}$$

Since the interaction (2) is of purely orbital nature, the spin $(\vec{S} + \vec{s})$ of the system is not affected. The orbital part of H_Z is diagonal in both the decoupled and coupled $(Ll)G$ representations. All symmetry properties referring to the orbital part of the wave function for the two-atom system are obtained from the derivations of Sec. II C 3 (in the coupled basis). As the field

effect will be important for $\mu_B B \sim \tau_c^{-1}$, this implies that the system is in the Paschen-Back regime and no recoupling of L and S is needed after collision. For $l = 0$ ground states, the symmetries are those given in (11).

c. General case. As H_Z is nondiagonal in the coupled basis, we use the uncoupled one and some minor modifications of the demonstrations of Sec. II B. The relations between $\{U_q^2\}$ coefficients are those given in the Appendix. The transformation in rotations and plane reflections of the uncoupled basis are given by[21]

$$R_Z(\gamma)|JM, jm\rangle = e^{-i\gamma(M+m)}|JM, jm\rangle \tag{21}$$

and

$$T(\xi)|JM, jm\rangle = (-)^{J+j-m-M} e^{2i\xi(M+m)}|J-M, j-m\rangle . \tag{22}$$

Using the invariance under exchange of atoms, we split Schrödinger's equation into two differential sets for the $+V$ and $-V$ potentials, the associated collision matrices being $\Sigma(+)$ and $\Sigma(-)$, connected by (10) to Σ_1 and Σ_2. The matrix elements of the interaction potential in the interaction picture are

$$\langle \pm J'M', j'm'|P|\pm JM, jm\rangle = \mp \frac{3}{R^3} \frac{\langle J'\|P\|j\rangle\langle j'\|P\|J\rangle}{[2J'+1]^{1/2}[2j'+1]^{1/2}} \exp\{i\omega x[g_f(m'-m)+g_e(M'-M)]\}$$

$$\times \sum_{q q_1 q_2} (-)^q U_{-q}^2(\varphi\theta\gamma\psi)\langle 11q_1q_2|2q\rangle\langle j1mq_1|J'M'\rangle\langle J1Mq_2|j'm'\rangle , \tag{23}$$

with

$$\langle \alpha'J'\|P^{(1)}\|\alpha j\rangle = \delta_{SS'}\langle n'L'\|P\|nl\rangle(-)^{1+j+L'+S}(2j+1)^{1/2}(2J'+1)^{1/2}\begin{Bmatrix} L' & 1 & l \\ j & S & J' \end{Bmatrix} .$$

Using $\langle L\|P\|l\rangle^* = (-)^{l-L}\langle l\|P\|L\rangle$, one deduces that $\langle L\|P\|l\rangle\langle l\|P\|L\rangle$ is real. Then relations (A1)–(A5) are still valid, and one can deduce the following relations for each class of atoms, where the g are obvious generalizations of (8) for *the two-atom system:*

$$g^{(M_1'm_2',p_1'p_2')(M_1m_2,p_1p_2)}(i)$$
$$= \delta(M_1'+m_2'+p_1+p_2-M_1-m_2-p_1'-p_2')g(i) , \tag{24a}$$

$$g^{(M_1'm_2',p_1'p_2')(M_1m_2,p_1p_2)}(i)$$
$$= g^{(M_1m_2,p_1p_2)(M_1'm_2',p_1'p_2')}(i) , \tag{24b}$$

$$g^{(M_1'm_2',p_1'p_2')(M_1m_2,p_1p_2)}(i) = g^{(p_1'p_2',M_1'm_2')(p_1p_2,M_1m_2)^*}(i) , \tag{24c}$$

$$g^{(M_1'm_2',p_1'p_2')(M_1m_2,p_1p_2)}(i)$$
$$= (-)^\alpha g^{(-M_1'-m_2',-p_1'-p_2')(-M_1-m_2,-p_1-p_2)^*}(i) , \tag{24d}$$

$$\alpha = \Sigma Ji - \Sigma Mi .$$

The (J, j) indices have been omitted for simplicity.

The interpretation of the relations is as in (11). For excitation transfer, one obtained the relations by substituting $M_1' = p_1'$, $m_2' = p_2'$, $M_1 = p_1$, and $m_2 = p_2$ into (24). For the relaxation of the whole ensemble of atoms, one has, moreover, the conservation law

$$\sum_{J_1'M_1', j_2'm_2'} g^{(J_1'M_1', j_2'm_2')(J_1M_1, j_2m_2)}(1+2) = 0 . \tag{25}$$

As (24d) comes from the effect of reflection, this relation will not be valid in the case of decoupling of $\vec{L}$ and $\vec{S}$ due to the field, since (22) no longer holds.

III. QUANTUM-MECHANICAL TREATMENT AND DETAILED BALANCE

A. Derivation of symmetry properties

Among the various relations established in the previous section with semiclassical arguments, some have a very simple interpretation using a

The mean rates of transfer between the internal state α_a and α_b of the particles are deduced from (33) by summation over the momenta of the in-going waves. Since $f(v_a)$ is the Maxwell-Boltzmann velocity distribution function of the atoms in the vapor, one has

$$\bar{g}^{(\alpha_b)(\alpha_a)} = \int f(v_a) v_a \sigma_{a \to b} \, dv_a. \tag{35}$$

Then using (33), (34), and $E^i(A\alpha) = E^i(\alpha)$, one obtains

$$\bar{g}_{(\alpha_b)(\alpha_a)} = \exp^{[-[E^i(\alpha_b)-E^i(\alpha_a)]/(kT)]} \bar{g}^{(A\alpha_a)(A\alpha_b)}, \tag{36}$$

which is detailed balance for a system submitted to an external magnetic field. This derivation supposes an isotropic Maxwell-Boltzmann velocity distribution function, i.e., that the collision process does not strongly perturb the velocity of the atoms.

With $(\alpha_a) = (Jm)$ and $(\alpha_b) = (Jp)$, (36) gives

$$\bar{g}^{(JpJp)(JmJm)} = e^{-(p-m)\hbar\omega/(kT)} g^{(JmJm)(JpJp)}, \tag{37}$$

which is of course reduced to (28) when $\hbar\omega \ll kT$. This permits one to fix the limit of validity of the semiclassical relations deduced in Sec. II.

a. Remarks. For excitation transfer between two sets (Jm) and $(J'm')$ of levels separated by the energy difference ΔE, in zero field time-reversal invariance leads to

$$\bar{g}^{(J'm'J'm')(JmJm)} = e^{-[E(J')-E(J)]/(kT)}$$
$$\times \bar{g}^{(J-mJ-m)(J'-m'J'-m')}, \tag{38}$$

which is not equivalent to (36). If the system possesses rotational invariance or invariance in plane reflections, this gives

$$\bar{g}^{(J'm'J'm')(JmJm)} = \bar{g}^{(J'-m'J'-m')(JmJm)}. \tag{39}$$

The combination of (38) and (39) produces a new relation equivalent to (37), although the hypotheses of the demonstration are different and the two previous relations do not hold separately in a strong magnetic field.

C. Symmetrizing semiclassical results

For small values of $\hbar\omega$ ($\hbar\omega < \frac{1}{10}kT$) and to avoid a totally quantum-mechanical treatment, one may try to extend the validity of the semiclassical approximation by introducing proper correction of the transfer rates in order to obtain a set of co-efficients approximately verifying detailed balance. We describe such a possibility of symmetrization, adapted from the work of Bates[26] and of Jamieson and Reid,[27] which allows the deduction of velocity-averaged transfer rates satisfying detailed balance.

But this method of symmetrizing is not unique,[26] and the main arguments for its use are its simplic-

ity and accuracy for electron-atom collisions.[27] Some aspects of the extension of the validity of the semiclassical approximation require a fully quantum-mechanical approach.

Semiclassical results are obtained for a given velocity v of the atoms. The principle of the method described here is to introduce into the semiclassical result for the probability of transition between m and p Zeeman sublevels a factor which takes into account the fact that the velocities v_m and v_p are different before and after collision. The simplest choice is to take v_m/v_p as a correction factor. Associated with the velocity v used in the semiclassical calculations, v_m and v_p are determined by energy conservation in the $m \to p$ process and by assuming the mean value is v. The symmetrized cross section is then

$$\tilde{\sigma}^{(pp)(mm)}(v_m) = (v_p/v_m)\sigma^{(pp)(mm)}(v), \tag{40}$$

and, using $\sigma^{(pp)(mm)}(v) = \sigma^{(mm)(pp)}(v)$, one obtains

$$v_p^2 \tilde{\sigma}^{(mm)(pp)}(v_p) = v_m^2 \tilde{\sigma}^{(pp)(mm)}(v_m), \tag{41}$$

which is just equivalent to (33) for the total energy E. After velocity averaging, the $\tilde{g}^{(mm)(pp)}$ coefficients then satisfy detailed-balance expression (37).

To relate the $\tilde{g}$ and $\bar{g}$ (unsymmetrized) velocity-averaged transfer rates, an approximate expression can be obtained at the limit $\hbar\omega \ll kT$ by developing the Maxwell-Boltzmann distribution function. So doing one obtains

$$\tilde{g}^{(pp)(mm)} = e^{-\hbar\omega(p-m)/(2kT)} \bar{g}^{(pp)(mm)}, \tag{42}$$

which is of course an obvious way to correct the results.

Symmetrization does not strongly affect relations (9) and (11). For $A^*(J=1)$-X collisions, one has $\bar{g}^{(11)(00)} \neq g^{(-1-1)(00)}$.[25] Then with (42)

$$\tilde{g}^{(11)(00)}/\tilde{g}^{(-1-1)(00)} = e^{-\hbar\omega/(kT)} \bar{g}^{(11)(00)}/\bar{g}^{(-1-1)(00)} \tag{43}$$

Following the attractive or repulsive character of the potential which governs the behavior of $\bar{g}^{(11)(00)}/\bar{g}^{(-1-1)(00)}$,[28] symmetrization will increase or decrease the effect of the magnetic field on the ratio of the transfer rates.[12] Of course, the separation into two kinds of effects is in some aspects arbitrary, and will not exist with a fully quantum-mechanical treatment of the problem. However, if $\hbar\omega \ll kT$, the effect of detailed balance is always small and $\bar{g}^{(11)(00)}/\bar{g}^{(-1-1)(00)}$ can be observed almost free from corrections.[28,29] Note that in zero field the ratio (43) is just 1.

For A^*-A resonant collisions ($J=1 \to j=0$ transitions) the semiclassical results obey an additional relation, (11d). In this case one obtains after symmetrization through (42)

quantum-mechanical treatment. Only one relation [(9d) or (11d)] connecting the evolution of the u and g states under exchange in A^*-A collisions or the evolution in the $+V$ and $-V$ potentials in A^*-X collisions does not have a quantum-mechanical analog. Of course a fully quantum-mechanical treatment of the $+V$ and $-V$ potentials does not give the same result as a rule.

The establishment of the properties due to statistical rotational invariance and Hermiticity of the density matrix is nearly obvious,[16] and leads to the semiclassical results Secs. III A 1 and III A 4. One can demonstrate the last property (9b) concerning the invariance in the product of XOZ-plane reflections and the time-reversal operation with a few additional hypotheses.[15] Our notation will be ρ_b for the density matrix of the bath H and Σ for the Hamiltonian and the collision matrix of the system K for the time-reversal operator T for the XOZ-plane reflection operation, and $A = KT$ for the antilinear operator product of these two operations. The following relations are then verified:

$$A\rho_b A^\dagger = \rho_b, \quad AHA^\dagger = H,$$

and

$$A^\dagger \Sigma^\dagger A = \Sigma. \tag{26}$$

The relaxation rates for the populations are given by

$$g^{(mm)(pp)} = \delta_{mp} - \mathrm{Tr}\{|Jm\rangle\langle Jm|\Sigma|Jp\rangle\langle Jp|\rho_b\Sigma^\dagger\}. \tag{27}$$

Using (26), one obtains with $A|Jm\rangle\langle Jm|A^\dagger = |Jm\rangle\langle Jm|$:

$$g^{(mm)(pp)} = \delta_{mp} - \mathrm{Tr}\{(A^\dagger\Sigma^\dagger|p\rangle\langle p|\rho_b\Sigma)(A|m\rangle\langle m|)\},$$

and by permuting the two antilinear operators in the trace

$$g^{(mm)(pp)} = \delta_{mp} - \mathrm{Tr}\{|p\rangle\langle p|\Sigma|m\rangle\langle m|\Sigma^\dagger\rho_b\},$$

To obtain the semiclassical equation (9b), one more approximation is needed viz., $[\Sigma, \rho_b] = 0$, which means that both the perturbation of the bath and the coupling with the system are weak. This is true, e.g., for a structureless perturber when the motion is modified weakly by the collision process, and for elastic collisions without energy transfer with perturbers whose internal and external states are isotropic. One then deduces

$$g^{(JmJm)(JpJp)} = g^{(JpJp)(JmJm)}. \tag{28}$$

This does not hold when the condition $\hbar\omega \ll kT$ is not fulfilled.

B. Detailed balance

Detailed balance with strong magnetic fields can be established with some modification of the usual demonstration. The transition matrix T which is used for this purpose is defined by[8]

$$T = \tfrac{1}{2}(i/\pi)(\Sigma - 1).$$

We specify the initial state a of the whole system by the ensemble of the internal variables α_a and the external degree of freedom ($\vec{k}_a$ being the wave number of the ingoing wave) and, similarly for the final state b, so that $(\alpha_b, \vec{k}_b)$ is the final state of the system.

The main problem in establishing detailed balance in a strong magnetic field arises from the lack of invariance in the system under the time-reversal operation. But this difficulty is easily overcome by noting that the Hamiltonian H of the system is invariant in the A operation defined in Sec. III A.

As the mathematical properties of A and K are the same, one can use the demonstration of Messiah[8] with A instead of K. It follows that

$$T_{Ab\to Aa} = T_{a\to b}, \tag{29}$$

which expresses the equality of the diffusion amplitudes for the direct process and the process deduced by the product of time-reversal operation and XOZ-plane reflection, for the same total energy E of the whole system.

The number of particles scattered per second in a unit solid angle in the $\vec{k}_b$ direction for a unit incident flux is then

$$\frac{d\sigma_{a\to b}}{d\Omega} = \frac{2\pi}{\hbar v_a}|T_{a\to b}|^2\rho_b(E), \tag{30}$$

where $\rho_b = m\hbar k_b/(2\pi\hbar)^3$ is the final-state density around E. For the inverse process, one has

$$\frac{d\sigma_{Ab\to Aa}}{d\Omega} = \frac{2\pi}{\hbar v_b'}|T_{Ab\to Aa}|^2\rho_{Aa}(E), \tag{31}$$

where v_b' is deduced from v_b by the A transformation and then is just the transformation of $(-\vec{v}_b)$ in XOZ-plane reflections.

Using (34) and the explicit expressions of $\rho(E)$, one obtains

$$(v_b'/v_a)d\sigma_{Ab\to Aa} = (v_a/v_b)d\sigma_{a\to b}. \tag{32}$$

The distribution of $\vec{k}_a$ wave vectors being supposed isotropic, one obtains after angular averaging

$$v_b^2\sigma_{Ab\to Aa}(E) = v_a^2\sigma_{a\to b}(E). \tag{33}$$

The total energy E is

$$E = E^i(\alpha_a) + \tfrac{1}{2}mv_a^2 = E^i(\alpha_b) + \tfrac{1}{2}mv_b^2, \tag{34}$$

where $E^i(\alpha_a)$ and $E^i(\alpha_b)$ are the internal energies of the atoms before and after the collision process when the interaction potential is negligibly small. Relation (33) is just the analog of relation $(XIV$-150) of Messiah,[8] provided one replaces K by A.

$$\tilde{g}^{(11)(00)} = \tilde{g}^{(00)(-1-1)} = e^{-\hbar\omega/(2kT)}\tilde{g}^{(11)(00)} ,$$

showing that the mean transfer rate $\frac{1}{2}(\tilde{g}^{(11)(00)} + \tilde{g}^{(-1-1)(00)})$ from $m = 0$ to $m = \pm 1$ is given by

$$\tilde{g}(m = 0 \rightarrow m = \pm 1) = \mathrm{ch}[\hbar\omega/(2kT)]\tilde{g}^{(11)(00)} , \qquad (44)$$

and is only weakly modified by the symmetrization procedure.[11]

IV. APPROXIMATE SEMICLASSICAL THEORY

The basic ideas of the method have been developed by Anderson,[30] by Tsao and Curnutte,[31] and by Omont.[25,32] They are in fact very similar to those adopted in the general theory of relaxation and correlation functions,[33] and so it is not surprising that some of the results we derive in the following have a very simple interpretation within the general framework of this theory.

A. Relaxation matrix for large impact parameters

The collision matrix Σ is given by[34]

$$\Sigma = T \exp[-ie^{iH_0 t}V_{12}(t)e^{-iH_0 t}] , \qquad (45)$$

where H_0 is the unperturbed Hamiltonian (including the Zeeman term, $\vec{L}\cdot\vec{S}$ structure, etc.), $V_{12}(t)$ the t-parametrized interaction potential, and T the chronological operator. In general, a second-order expansion of (45) in V_{12} is sufficient for both accuracy and simplicity. But higher-order terms may give evidence of some peculiar properties, such as, for example, the lack of invariance under time reversal.[28] The second-order expansion valid for large impact parameters is given by

$$\begin{aligned}
\Sigma = 1 &- i \int_{-\infty}^{+\infty} dt \, e^{iH_0 t}V_{12}e^{-iH_0 t} \\
&- \int_{-\infty}^{+\infty}\int_{-\infty}^{t} dt \, dt' e^{iH_0 t}V_{12}(t)e^{-iH_0(t-t')} \\
&\times V_{12}(t')e^{-iH_0 t'} ,
\end{aligned} \qquad (46)$$

the diagrammatic interpretation of which is quite obvious. For A^*-X collisions, (46) gives exactly the approximate collision matrix. For A^*-A collisions, owing to the peculiar symmetry properties of dipole-dipole interaction it is easy to draw from (46) the expressions of the Σ_1 and Σ_2 collision matrices for each class of atoms.[11,25] The terms with an even number of interactions make up Σ_1, while Σ_2 is composed of terms with an odd number of interactions.

The asymptotic expansion of the relaxation matrix $\langle\mathfrak{M}(b,v)\rangle$ for a given velocity and large impact parameter is then obtained by retaining the terms in $\Sigma\rho\Sigma^\dagger$ consistent with the degree of approximation in (46) and after angular averaging. The relaxation matrix $\langle\mathfrak{M}(b,v)\rangle$ can be completely express-

ed[11,12,32] in terms of the Fourier transform $f(\eta)$ of the symmetrical correlation function[35] $S(x,x')$ of the interaction potential $V(x)$ given by

$$\begin{aligned}
S(x,x') &= \mathrm{Tr}[V(x)V^\dagger(x')] \\
&= \sum_{q_1}(-)^{q_1}U_{q_1}^2(x)U_{-q_1}^2(x') ,
\end{aligned} \qquad (47)$$

with

$$f(\eta) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} dx \, dx' \, e^{i\eta(x-x')}S(x,x') , \qquad (48)$$

$$f(0) = 1 .$$

The asymptotic values of the relaxation rates are expressed in terms of $f(\eta)$ and their imaginary parts (shifts of the lines) in terms of Cauchy's principal value of $f(\eta)$. For large impact parameters, the transfer rates for the population then take the form

$$\Pi^{AS}(b) = \alpha q^2 f(\eta) , \qquad (49)$$

where q is the strength of the interaction depending in reduced variables on b and v, and $\eta = \Delta E\, b/v$, where ΔE is the energy difference between the two states considered in the process.

B. Cutoff approximation for small impact parameters

To calculate transfer rates one uses Eq. (49) for $b > b_c$ and for $b < b_c$, the value $^0\Pi$ constant with b which may be determined by various approximations,[32,36] for example, total redistribution of excitation, adiabatic approximation. The determination of the Weisskopf radius b_c in zero field is done by writing

$$\Pi^{AS}(b_c) = {}^0\Pi = \mu^A\, {}^0\Pi\, q^2 . \qquad (50)$$

Then $q_c^2\mu^A = 1$, where μ^A is an angular factor which depends on the process under consideration.[7,25] For dipole-dipole interaction[14] ($q \propto 1/b^2 v$) the transfer rates for population are proportional to the K coefficient defined by[14]

$$K(0) = \int \Pi(q)\, d\left(\frac{1}{q}\right) = 2(\mu^A)^{1/2}\, {}^0\Pi . \qquad (51)$$

C. Cutoff radius in nonzero field

The $^0\Pi$ value may be determined either from physical arguments or by assuming that the $K(0)$-computed transfer rate (when available) coincide exactly with (51). For not-too-strong magnetic fields, one can admit that the $^0\Pi$ value is not modified by the effect of the field. As Π^{AS} depends on the field strength, the cutoff radius will be modified, and is given by

$$\Pi^{AS} = {}^0\Pi\, \mu^A\, q_c^2 f(\eta_c) = {}^0\Pi .$$

Then b_c or, equivalently, q_c is given by the implicit equation

$$f(\eta_c) = 1/(q_c^2 \mu^A).\qquad(52)$$

For dipole-dipole interaction, (51) then becomes[25]

$$\Phi(B) = K(B)/K(0) = \tfrac{1}{2}[f(\eta_c)]^{1/2}[1 + F_1(\eta_c)/f(\eta_c)],\qquad(53)$$

where F_1 is the integral of $f(\eta)$ over q. The field dependance of the rates of transfer with B are completely determined by (52) and (53). The functions f and F_1 have been determined analytically for a great variety of potentials.[31,37-39] For dipole-dipole interaction, they are explicitly (the K_i being modified Bessel functions[40])

$$f(\eta) = \tfrac{1}{4}\eta^4[K_2^2(\eta) + 4K_1^2(\eta) + 3K_0^2(\eta)],$$

$$F_1(\eta) = \tfrac{1}{4}\eta^4[K_3(\eta)K_1(\eta) + 4K_2(\eta)K_0(\eta) - K_2^2(\eta)$$
$$- K_1^2(\eta) - 3K_0^2(\eta)],$$

and are tabulated with Φ in Table I. For the R^{-6} Van der Waals interaction, $f(\eta)$ is just a combination of exponential and powers.[12,31,41]

D. Some remarks

1. Remarks on symmetries

As the method is based on second order perturbation theory, one can easily show that the symmetry properties of $\langle \mathfrak{M} \rangle$ are greater in number than those predicted in the preceding sections.[42] Some anisotropy effects already exist, but coupling between tensorial components of the density matrix occur in general at higher orders of the development.[28]

2. Case of several evolution frequencies with the field

In general, the physical quantities of interest are combinations of elementary processes i which evolve at different frequencies with the field.[43] These various processes cannot be distinguished in zero magnetic field, which means that only one cutoff radius has to be used. We suppose, for example, that we have

$$\Pi^{AS}(b) = q^2 \left(\sum_i \Pi^i(B=0) \right) \sum_i d_i f(\alpha_i \eta),\qquad(54)$$

with

$$\sum_i d_i = \sum_i \Pi^i(0) / \left(\sum_i \Pi^i(0) \right) = 1,$$

instead of (49). The method of Sec. IV C gives in this case

$$\sum_i d_i f(\alpha_i \eta) = 1/(q_c^2 \mu^A),\qquad(55)$$

$$\Phi(B) = \frac{1}{2}\left(\sum_i d_i f(\alpha_i \eta_c) \right)^{1/2}\left(1 + \frac{\sum_i d_i F_1(\alpha_i \eta_c)}{\sum_i d_i f(\alpha_i \eta_c)} \right)\qquad(56)$$

TABLE I. Values of the Fourier transform of the correlation function $f(x)$ [Eq. (48)] and field dependence of the transfer rates for R^{-3} dipole-dipole interaction. The solution of the set of implicit equations (52) and (53) giving the field dependence is obtained by first identifying $x[f_1(x)]^{-1/4}$ and the field parameter τ [giving Eq. (52)] and then computing Φ through (53).

$x[f_1(x)]^{-1/4}$	x	$f_1(x)$	$F_1(x)$	$\Phi(\tau)$
0	0	0	1	1
0.1	0.1	1.01	1.02	1.010
0.199	0.2	1.02	1.05	1.025
0.296	0.3	1.05	1.07	1.034
0.393	0.4	1.07	1.08	1.039
0.488	0.5	1.10	1.07	1.035
0.582	0.6	1.13	1.05	1.025
0.676	0.7	1.15	1.02	1.012
0.771	0.8	1.16	0.974	0.991
0.867	0.9	1.16	0.924	0.967
0.964	1	1.16	0.869	0.942
1.065	1.1	1.14	0.811	0.914
1.169	1.2	1.11	0.750	0.883
1.275	1.3	1.08	0.690	0.852
1.386	1.4	1.04	0.631	0.819
1.502	1.5	0.994	0.574	0.786
1.623	1.6	0.945	0.519	0.753
1.749	1.7	0.892	0.467	0.719
1.882	1.8	0.837	0.419	0.686
2.020	1.9	0.782	0.374	0.654
2.167	2	0.726	0.333	0.621
2.319	2.1	0.672	0.296	0.590
2.481	2.2	0.618	0.262	0.560
2.651	2.3	0.567	0.231	0.530
2.829	2.4	0.518	0.203	0.501
3.018	2.5	0.471	0.178	0.473
3.216	2.6	0.427	0.156	0.446
3.425	2.7	0.386	0.136	0.420
3.646	2.8	0.348	0.119	0.396
3.877	2.9	0.313	0.103	0.372
4.120	3.0	0.281	0.0898	0.350
4.380	3.1	0.251	0.0780	0.328
4.641	3.2	0.224	0.0675	0.308
4.941	3.3	0.199	0.0584	0.289
5.242	3.4	0.177	0.0504	0.270
5.560	3.5	0.157	0.0434	0.253
5.896	3.6	0.139	0.0374	0.237
6.261	3.7	0.122	0.0374	0.221
6.629	3.8	0.108	0.026	0.206
7.030	3.9	0.0947	0.0237	0.192
7.448	4.0	0.0832	0.0203	0.179

by defining only one cutoff radius for the whole process in strong field, and then insuring self-consistency with the zero-field treatment.

There is nevertheless another way to evaluate the relaxation rates, by defining a cutoff radius for each elementary process, i giving then

$$f(\alpha_i \eta_i^c) = 1/(q_c^{2i} \mu^i)\qquad(57)$$

and

$$\Phi(B) = \frac{1}{2} \frac{\sum_i (\mu^i)^{1/2} \, {}^0\Pi^i [f(\alpha_i \eta_c^i)]^{1/2}}{\sum_i (\mu^i)^{1/2} \, {}^0\Pi^i}$$

$$\times \left(1 + \frac{F_1(\alpha_i \eta_c^i)}{f(\alpha_i \eta_c^i)}\right) . \qquad (58)$$

Of course these two evaluations are not equivalent, and give different predictions for $B = 0$ and $B \neq 0$. One can only demonstrate that (56) is a majorant of (58) for $B = 0$. In practical cases, calculations show that the predictions of (56) and (58) are not far from each other.

3. Conclusions

The method discussed in this section has some interest, as it avoids such very complicated procedures as those involved for collisions in strong magnetic fields. In some cases, it gives very bad predictions, such as for the excitation transfer between two isotopes[7,44] (the $^0\Pi$ values are then strongly dependant on the energy difference ΔE between levels). But, as will be shown in the Sec. V and paper,[45] it gives in general a good estimation for the variation of the transfer rates for resonant collisions in strong magnetic fields. In spite of a systematic overestimation of the cross sections and its multiform character (pointed out in Sec. IV D 2), it permits in some special cases a good understanding of the experimental results, and is very useful for qualitative purposes. For example, the interpretation in terms of correlation function makes clearer the notion of correlation time τ_c associated with the potential. Varying the field is then in some aspects equivalent to making a Fourier analysis of the potential.

V. EXACT SOLUTIONS FOR $A*-A$ AND $A*-X$

The solutions of various classes of problems have been obtained by solving Schrödinger's equation with appropriate methods for $J = 1 \rightarrow J = 0$ resonance transitions in the case of identical atoms[11] (R^{-3} dipole-dipole interaction) and for the interaction via R^{-6} Van der Waals potential of a $J = 1$ excited atom with a structureless partner.[12,25]

Symmetries have been checked for each $(B, b, v, \theta, \varphi, \gamma)$ value used in numerical integration. They are at each step in exact agreement with the predictions of Sec. II and of Sec. IV for large impact parameters and ultimately provide tests of accuracy and methods for considerable reduction of computation time.

A. Anticrossing of energy levels

Some results of the numerical studies need to be stressed. In zero magnetic field, the collision process is equivalent in some aspects to the for-
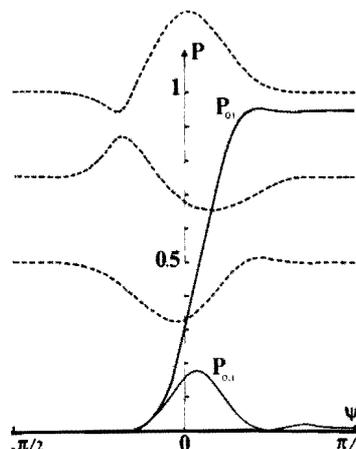

FIG. 1. Correlations between transition probabilities and potential-energy curves during the collision. The situation corresponds to R^{-6} anisotropic Van der Waals interaction with a sign such that $E_\Sigma > E_\pi$ in zero magnetic field. The field belongs to the collision plane and is parallel to the second bisector plane of $(\vec{b}, \vec{v})$ $(\theta = \frac{1}{2}\pi, \varphi = \frac{1}{4}\pi)$. The strength of the field corresponds to a Zeeman splitting of about $2\tau_c^{-1}$, and the impact parameter is about four times the Weisskopf radius. At $\psi = -\frac{1}{2}\pi$ $(t = -\infty)$ the system is in the $m = 0$ substate. The $P_{0\pm1}$ full curves represent the probabilities of finding the system in the $m = \pm 1$ substates during the collision. The dashed curves (arbitrary units) represent the eigenvalues of the time-dependent Hamiltonian. At $\psi = \pm\frac{1}{2}\pi$ they correspond to the purely Zeeman case. Potential-energy curves anticrossing partly explain the strong value of P_{01} at the end of the collision process, but the increase of $P_{01}(\psi)$ is not well localized near this point.

mation of a quasimolecule. For a $J = 1$ atomic state, the associated molecular states are Π states and one Σ state. Due to the symmetry of the electrostatic interaction, the two Π states are degenerate for all internuclear distances. The evolution of the Π state "perpendicular to the collision plane" is not coupled to the evolution of the Π and Σ states belonging to the collision plane.[7] Moreover, the potential-energy curves are invariant in the $X \rightarrow -X$ transformation.

When a magnetic field is applied to the system, this fundamental Kramers degeneracy no longer exists. Potential-energy curve anticrossing appears as in Fig. 1, where the curves are no longer invariant in the $X \rightarrow -X$ transformation. This results from the breaking of Kramers degeneracy due to the Zeeman Hamiltonian. The spectrum is then characteristic of a Zeeman effect at large internuclear distances and of a Stark effect for $X \approx 0$. Correlation studies of potential-energy curves and transition probabilities between Zeeman sublevels have been done.[46] They reveal that the presence of anticrossings is not always corre-
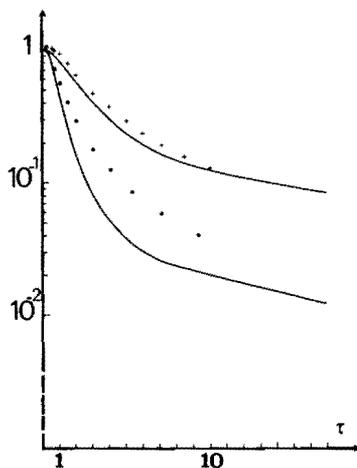
FIG. 2. R^{-3} dipole-dipole interaction between identical atoms. Field variations (logarithmic scale) of the $m = 0 \rightarrow m = \pm 1$ and $m = \pm 1 \rightarrow m = \mp 1$ transfer rates for the whole $1 + 2$ ensemble of atoms (reduced to the zero-field value). The parameter τ is just $g_J \mu_B B p^{1/2} v^{-3/2}$, where p is proportional to the oscillator strength of the resonance transition. The predictions of Eq. (53) using the symmetrical correlation function for the potential are represented by $+$ for the $M = 0 \rightarrow M = \pm 1$ and by $\bullet$ for the $M = \pm 1 \rightarrow M = \mp 1$ transfer rates.

lated with a strong increase in the transition probability between the unperturbed atomic sublevels. But on the other hand the very special shape of the energy diagram is connected with the existence of strong anisotropy effects at the end of the collision process between, e.g., the populations of the $m = +1$ and $m = -1$ Zeeman sublevels of the atoms (Fig. 1). These effects do not exist in zero magnetic field. Such effects are also properly taken into account by an asymptotic expansion of the $\langle \mathfrak{M} \rangle$ relaxation matrix[28] of third order in V. These features are of particular interest for beam-beam experiments for which very strong anisotropy effects can be predicted. They also present a very strong analogy with the behaviors observed in collision-induced rotational transitions between molecules and atoms for odd values of the variations Δj of the rotational quantum number.[47]

B. Results

The field variations of the Zeeman transfer rates (reduced to the zero-field value) are given in Figs. 2 and 3 for, respectively, R^{-3} dipole-dipole interaction and R^{-6} Van der Waals interaction. The proper definitions of τ are given in the figure captions. For R^{-3} dipole-dipole interaction, τ is proportional[11] to $Bv^{-3/2}$ and for R^{-6} interaction to $Bv^{-6/5}$.[12] Physically the parameters are proportional to the product $\Delta E \tau_c / \hbar$ and directly measure the importance of the resonance defect
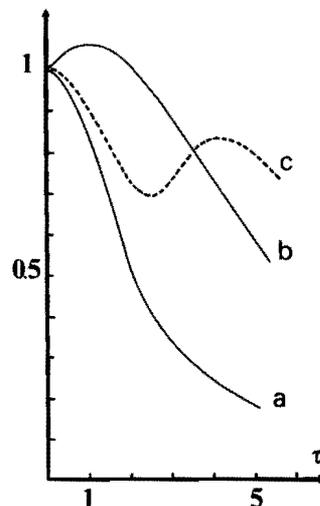

FIG. 3. R^{-6} anisotropic Van der Waals interaction. Field variations (reduced to the zero-field value) of the $m = 0 \rightarrow m = \pm 1$ and $m = \pm 1 \rightarrow m = \mp 1$ transfer rates. The parameter τ is just $g_J \mu_B B p^{1/5} v^{-6/5}$, where p is the anisotropy parameter of the potential related to the product of the polarizability of the perturbers and to the mean value of $\langle r^2 \rangle$ for the $J = 1$ excited atom: (a) $m = \pm 1 \rightarrow m = \mp 1$, (b) $m = 0 \rightarrow m = -1$, and (c) $m = 0 \rightarrow m = 1$. The situation corresponds to a zero-field position of potential-energy curves such that $E_\Sigma < E_\Pi$. The inverse situation $E_\Sigma > E_\Pi$ is obtained by interchanging only the signs of m in (b) and (c) because of scaling laws for the problem.

compared to the width of the Fourier transform of the correlation function of the potential, which for these slowly varying potentials is approximately the inverse of a mean collision time.

1. R^{-3} potential

The semiclassical $(m = 0 \rightarrow m = \pm 1)$ transfer rates are identical for all field values, a phenomenon connected with the (u, g) separability of Schrödinger's equation. In zero field, the rates are velocity independent for a semiclassical straight-line trajectory formulation.[48,49] This is almost true in a quantum-mechanical approach to the problem.[49] In a nonzero magnetic field, the rates are velocity dependent via the τ parameter.[7,11,50]

In Fig. 2 we have plotted the predictions obtained with the method of Sec. IV. At some field values this leads to a 20%–100% overestimation of the transfer rates, especially for $m = \pm 1 \rightarrow m = \mp 1$ transitions. For $m = 0 \rightarrow m = \pm 1$ transitions the approximation is not too bad and gives a first estimate of the variations with the field.

2. R^{-6} potential

The semiclassical $(m = 0 \rightarrow m = \pm 1)$ transfer rates are different as a result of the action of the mag-

netic field during the collision process.[12,28] As
the effect depends on the sign of the anisotropic
part of the potential, i.e., on the relative positions
of the Σ and Π potential-energy curves during the
collision, this is a way of determining the sign of
the anisotropic part. Experimental verifications
of this behavior for Hg* $(6\,^3P_1)$-rare gas collisions
in 200-kG magnetic fields have been reported[29]
and have shown qualitative agreement with pre-
dictions,[12,28] allowing one to determine the quali-
tative distribution of potential-energy curves for
such collisions at thermal energy. Experimental
verification of detailed balance has also been re-
ported.[29]

VI. CONCLUSION

Some theoretical aspects of the use of high mag-
netic fields for probing inelastic-collisional ex-
citation transfer have been described for thermal
collisions in a vapor, in conditions of broad line
excitation of the atoms. It will be of interest to
extend the analysis to the case of monomode nar-
row-laser-line excitation for the study of weakly
inelastic velocity-changing collisions,[51] as the
magnetic field seems to provide a convenient tool
for testing the velocity kernel and the memory
function.

APPENDIX: RELATIONS BETWEEN SEMICLASSICAL COLLISION MATRICES

1. Explicit form of the interaction potential

The $\{u_q^2(x)\}$ coefficients associated with a given
collision process $(\varphi\theta\gamma)$ satisfy the following re-
lations:

$$u_2^2(x) = u_{-2}^{2*}(x) = u_{-2}^2(-x) = \tfrac{1}{2}(1+ix)^2/r^2 \ ,$$

$$u_{\pm 1}^2(x) = 0, \quad u_0^2(x) = -1/\sqrt{6} \ ,$$

with $x = vt/b$, and are characteristic of the assum-
ed symmetries of the potential. The explicit form
of the $\{U_q^2(\varphi\theta\gamma x)\}$ in (3) is then given with U_q^{2*}
$= (-)^q U_{-q}^2$ (the Hermiticity of V) by

$$U_2^2(\varphi\theta\gamma x) = \tfrac{1}{4}e^{-2i\gamma}\big[(1+\cos^2\theta)\cos 2(\psi-\varphi) - \sin^2\theta$$
$$+ 2i\,\sin 2(\psi-\varphi)\cos\theta\big],$$

$$U_1^2(\varphi\theta\gamma x) = -\tfrac{1}{2}e^{-i\gamma}\big[\cos 2(\psi-\varphi)\cos\theta + \cos\theta$$
$$+ i\,\sin 2(\psi-\varphi)\big],$$

$$U_0^2(\varphi\theta\gamma x) = \tfrac{1}{4}\sqrt{6}\,\big[\sin^2\theta\cos 2(\psi-\varphi) + \sin^2\theta - \tfrac{2}{3}\big],$$

where $\psi = \arctan x$ is the angle of rotation of the
internuclear axis during the collision. When there
is no $\vec{L}\,\vec{S}$ decoupling by the field, Schrödinger's
equation in the interaction picture is just given by
Eqs. (5) and (6).

2. Relations between semiclassical collision matrices $\Sigma(\varphi\,\theta\,\gamma)$

Using the projection of (5) on a standard OZ
basis and the properties of $\{U_q^2\}$ coefficients, one
deduces several relations between collision ma-
trices associated with various orientations of the
collision planes relative to the field. Of course,
we do not consider the transformations that leave
$U^{(2)}$ invariant but associated with the same colli-
sion process either by changing only the set $(\varphi\theta\gamma)$
of Euler angles into an equivalent one of different
determination[8] or by changing the sense of the
collision frame. This does not lead to any new
relations, and P is now the representation of P
defined in (6) in the standard basis.

a. Transformation $\varphi \to \varphi + \pi$, $P(x, \pi+\varphi, \theta, \gamma)$
$= P(x, \varphi, \theta, \gamma)$. The two physical trajectories are
connected with a parity operation, leaving the
magnetic field unchanged. This together with (5)
gives

$$\Sigma(\varphi, \theta, \gamma) = \Sigma(\pi+\varphi, \theta, \gamma) \ . \tag{A1}$$

b. Transformation $(\varphi\theta\gamma) \to (\pi-\varphi, \theta, -\gamma, -x)$.
There $U_q^2(\pi-\varphi, \theta, -\gamma, -x) = U_q^2(\varphi\theta, \gamma x)^*$. As the
representations of $^{JJ'}T^{(k)}$ operators are real
matrices in a standard basis, one deduces that

$$P(-x, \pi-\varphi, \theta, \gamma) = P(x, \varphi, \theta, -\gamma)^* \ ,$$

and after elementary algebra

$$\Sigma(\varphi\theta\gamma) = \tilde{\Sigma}(\pi-\varphi, \theta, -\gamma) \tag{A2}$$

or equivalently with (A1)

$$\Sigma(\varphi, \theta, \gamma) = \tilde{\Sigma}(2\pi-\varphi, \theta, -\gamma).$$

These relations correlate the results of two colli-
sions with trajectories corresponding in XOZ-
plane reflections at reversed time x. Note that in
each transformation the field is not invariant but
only in the product.

c. OZ rotations. The rotation $R_z(\beta)$ around the
Z axis leads to

$$R_z(\beta)P(x\varphi\theta\gamma)R_z^\dagger(\beta) = P(x, \varphi, \theta, \gamma-\beta) \ ,$$

then to

$$\Sigma(\varphi, \theta, \gamma-\beta) = R_z(\beta)\Sigma(\varphi\theta\gamma)R_z^\dagger(\beta) \ , \tag{A3}$$

expressing the fact that the physical problem does
not depend on all three angles, but only on φ and θ.

d. $ZO\xi$-plane reflections. With $\vec{\xi}$ the vector of
polar angle ξ in the XOY plane and $T(\xi)$ the matrix
representation of the operator associated with
$ZO\xi$-plane reflections, one has

$$T(\xi)T_q^k T^\dagger(\xi) = (-)^{k+q}e^{2iq\xi}T_{-q}^k \ ,$$

leading to

$$T(\xi)P(x\varphi\theta\gamma)T^\dagger(\xi) = P(x, \varphi, \theta, \gamma+2\xi)^* \ .$$

Algebraic manipulation of Eq. (15) then produces

$$\Sigma(\pm, \varphi, \theta, \gamma) = T(\xi)\Sigma(\mp, \varphi, \theta, \gamma + 2\xi)* T^{\dagger}(\xi) , \quad (A4)$$

where the ($\pm$) refer to the cases in which the potential is $+P$ or $-P$. Equation (A4) permits the relation of solutions of Schrödinger's equation for two opposite potentials. Physically, this means that within the above-mentioned approximations, (A4) offers the possibility of obtaining collision matrices for potentials of opposite anisotropy in the case of A^*-X collisions (inverse relative positions of the potential-energy curves) when the solution is known for one sign. For A^*-A collisions between identical atoms Schrödinger's equation is invariant under atom exchange. Knowing the solution of (5) for the symmetric states, for example one can solve the collision problem completely by obtaining from (A4) the evolution of the antisymmetric states under exchange.

e. Unitarity. From $V = V^{\dagger}$, one deduces

$$\Sigma \cdot \Sigma^{\dagger} = I . \quad (A5)$$

3. Comparison to the zero-field case

Assuming statistical spherical symmetry, one can express the collision matrix in zero magnetic field by

$$\Sigma(\varphi\theta\gamma) = R(\varphi\theta\gamma)\Sigma(0, 0, 0)R^{\dagger}(\varphi\theta\gamma)$$

with $\Sigma(0, 0, 0) = \bar{\Sigma}(0, 0, 0)$ resulting in the same standard basis from invariance under the time-reversal operation and reflections in the trajectory plane,[6,7] $\Sigma(\pm) = \Sigma(\mp)^*$ and other, accidental symmetries in some cases as decoupling of (5) into two independent subsets of differential equations due to the particular form of V, which only allows coupling between $\Delta m = 0, \pm 2$ states.[25]

For nonzero magnetic field, the breakdown of rotational invariance formulated in (A6) is partially mitigated by other kinds of relations, which connect different collision processes in space and are closely related to the symmetries of the interaction potential and Zeeman Hamiltonian. But except in some special situations (e.g., when the collision planes are perpendicular to the field) one cannot in this situation find any relationship (except A5) for a given collision (φ, θ, γ) which permits simplification of the computation of $\Sigma(\varphi, \theta, \gamma)$.

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