Prototype model for nuclear spin conversion in molecules: The case of ”hydrogen”.

L.V.II’ichov *

Institute of Automation and Electrometry SB RAS,
Novosibirsk State University,
Novosibirsk 630090, Russian Federation

Abstract

Using the conception of the so-called quantum relaxation, we build a semiphenomenological model for ortho-para conversion of nuclear spin isomers of hydrogen-type molecule.

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1 Introduction

Recently an idea was proposed [1] and proved [2-4] that the combined action of intramolecular dynamics and environment could account for conversion of nuclear spin modifications of $^{13}CH_3F$. One may assume the same conversion mechanism for other molecules. This mechanism resides in the following. The intramolecular Hamiltonian is nondiagonal with respect to definite total nuclear spin $I$. That implies the nutations between molecular states with various $I$ values. The role of the environment is in the braking of nutation’s phase. Therefore the environment alone does not initiate transitions with nuclear spin value changing, but, destructing quantum coherence, the environment brakes the reversibility of nutations. It is remarkable that no cross-section can be ascribed to such a conversion way, which makes pointing a classic analogy to this quantum process rather problematic. For this reason, we name it quantum relaxation. The known phenomena of enantiomers conversion [5], decay of neutral kaons [6], and neutrino oscillations [7] are other examples of quantum relaxation.

Considered as quantum relaxation, the nuclear spin conversion delivers a number of interesting problems, especially when being extended beyond the lowest approximations with respect to the
spin-mixing intramolecular Hamiltonian. This was shown in the work [8], where quantum relaxation of multilevel system was considered in the context of rather general approach. The price paid for the progress, was also rather high. It consisted of specific form of intramolecular Hamiltonian which mixed only a pare of states belonging to various spin modifications. The dissipative term in the quantum evolution equation, was particular as well, being a modification of BGK collision model.

In the present work an attempt is made to overcome these limitations in the special case of hydrogen-type molecule. The success of such an approach is stipulated by specific algebraic properties of operators governing the evolution of nuclear spin and molecular frame. The author states by no means the quantum relaxation being the main (or even significant) cause for conversion of real ortho- and para-hydrogen. We consider \( H_2 \)-type-molecule because of the following three reasons:

1. due to its simplicity \( H_2 \)-molecule turns to be an ideal testing site for models of the influence of the environment and for investigation of sensitivity of the conversion rate to the variety of the models;
2. one can write the most general form for the intramolecular nuclear spin-mixing Hamiltonian allowable for \( H_2 \);
3. it is possible to account and to some extent investigate analitically higher orders of the spin-mixing interaction in the conversion process.

In Sec.2 and Sec.3 we introduce the set of operators for, respectively, nuclear spin subsystem and molecular frame. In what follows (Sec.4 and below) these operators are used as building blocks for construction of spin-mixing Hamiltonian and various dissipative terms.

2 Operator algebra of nuclear spin subsystem

The operators acting in the nuclear spin space of \( H_2 \) molecule are expressed through the protons’ spin operators \( \hat{I}^{(1)} \) and \( \hat{I}^{(2)} \) and may be considered as a basis of a 16-dimentional associative algebra. Let us introduce and describe its elements. This algebra includes naturally the three components of the total nuclear spin vector \( \hat{I} = \hat{I}^{(1)} + \hat{I}^{(2)} \). The total spin magnitude may take two values - 0 and 1. One may introduce the operator of the nuclear spin value \( \hat{I} \):

\[
\hat{I} = \frac{3}{4} + \left( \hat{I}^{(1)} \cdot \hat{I}^{(2)} \right).
\]

with the mentioned eigenvalues. This operator satisfies the evident relation \( (\hat{I} \cdot \hat{I}) = \hat{I} (\hat{I} + 1) \). We will either need raising and lowering operators with respect to \( \hat{I} \). Not too stretched manipulations provide the following vector operators

\[
\hat{I}^{(\pm)} = \hat{I}^{(1)} - \hat{I}^{(2)} \pm 2i \left( \hat{I}^{(1)} \times \hat{I}^{(2)} \right)
\]

with the needed properties, which is evident from the commutators

\[
[\hat{I}^{(\pm)}, \hat{I}] = \mp \hat{I}^{(\pm)}.
\]
Repeated application of any rising and lowering operators’ components gives zero:

\[ \hat{I}_i^{(+)}\hat{I}_j^{(+)} = \hat{I}_i^{(-)}\hat{I}_j^{(-)} = 0. \]  

(2.4)

One has also

\[ \hat{I}^{(-)} \hat{I}^{(+)} = \hat{I}^{(+)}\hat{I} = 0, \]  

(2.5)

and, respectively,

\[ \hat{I}^{(+)} \hat{I}^{(+)} = \hat{I}^{(+)}\hat{I} = \hat{I}^{(-)}. \]  

(2.6)

The products of raising and lowering operators’ components give

\[ \hat{I}_i^{(-)}\hat{I}_j^{(+)} = 4\delta_{ij}(1 - \hat{I}), \]  

(2.7)

where a new tensor operator

\[ \hat{P}_{ij} = \hat{I}_i^{(1)}\hat{I}_j^{(2)} + \hat{I}_j^{(1)}\hat{I}_i^{(2)} - \frac{2}{3}\delta_{ij} \left( \hat{I}_i^{(1)} \cdot \hat{I}_j^{(2)} \right) \]  

appears. This operator is at the same time symmetric traceless tensor in 3D space. Supplemented by unit, the set \( \{\hat{I}, \hat{I}, \hat{I}^{(+)}, \hat{I}^{(-)}, \hat{P}_{ij}\} \) forms the associative algebra of the nuclear spin subsystem of \( H_2 \).

The following product relations involving \( \hat{P}_{ij} \) will be needed:

\[ \hat{P}_{ij}\hat{I}_k^{(+)} = \frac{1}{3}\delta_{ij}\hat{I}_k^{(+)} - \frac{1}{2}\delta_{jk}\hat{I}_i^{(+)} - \frac{1}{2}\delta_{ki}\hat{I}_j^{(+)}, \]

\[ \hat{I}_k^{(-)}\hat{P}_{ij} = \frac{1}{3}\delta_{ij}\hat{I}_k^{(-)} - \frac{1}{2}\delta_{jk}\hat{I}_i^{(-)} - \frac{1}{2}\delta_{ki}\hat{I}_j^{(-)}, \]

\[ \hat{P}_{ij}\hat{I}_k^{(-)} = \hat{I}_k^{(+)}\hat{P}_{ij} = 0. \]  

(2.9)

To finish the set of products which will be used, one should add

\[ \hat{I}_i\hat{I}_j^{(+)} = i\epsilon_{ijk}\hat{I}_k^{(+)}; \quad \hat{I}_i\hat{I}_j = i\epsilon_{ijk}\hat{I}_k^{(-)}; \]

\[ \hat{I}_i\hat{I}_j^{(-)} = \hat{I}_i^{(+)}\hat{I}_j = 0. \]  

(2.10)

All other operator products are not of interest to us in the present work.
3 Operator algebra of molecular frame

It was shown in [9] that the evolution of molecular rotator could be described within the framework of 10-dimensional space spanned by the operator set \( \{ \hat{J}, \hat{J}, \hat{J}^+, \hat{J}^- \} \) which is at the same time the Lie algebra of the real symplectic group \( Sp(4, \mathbb{R}) \) or, speaking more precisely, of its simply connected covering metaplectic group \( Mp(4, \mathbb{R}) \) [10]. Here \( \hat{J} \) is the molecular rotational angular momentum; \( \hat{J} \) is the angular momentum operator value, so that \( (\hat{J} \cdot \hat{J}) = \hat{J}(\hat{J} + 1) ; \hat{J}^+ \) and \( \hat{J}^- = \hat{J}^+ \dagger \) are vector operators responsible, respectively, for transitions \( J \mapsto J \pm 1 \).

The structure of the metaplectic Lie algebra is characterized by the following set of commutators:

\[
[\hat{J}_i, \hat{J}_j] = i \epsilon_{ijk} \hat{J}_k, \quad [\hat{J}_i, \hat{J}_j^{(+)}] = i \epsilon_{ijk} \hat{J}_k^{(+)} \quad \text{and} \quad [\hat{J}_i, \hat{J}_j] = 0;
\]

\[
[\hat{J}_i^{(+)}, \hat{J}_j^{(-)}] = -\delta_{ij}(2\hat{J} + 1) - 2i \epsilon_{ijk} \hat{J}_k, \quad \downarrow \quad \text{(3.1)}
\]

\[
[\hat{J}_i^{(+)}, \hat{J}_j^{(+)}] = [\hat{J}_i^{(-)}, \hat{J}_j^{(-)}] = 0, \quad [\hat{J}^{(+)}, \hat{J}] = \mp \hat{J}^{(\pm)}.
\]

We need also the rules of \( \hat{J}^{(+)} \) and \( \hat{J}^{(-)} \) operation in the basis set of molecular rotational states \( \{|J, M\} \):

\[
\begin{align*}
\hat{J}_i^{(+)}|J, M\rangle &= -\sqrt{(J + M + 1)(J + M + 2)}|J + 1, M + 1\rangle, \\
\hat{J}_i^{(-)}|J, M\rangle &= -\sqrt{(J - M + 1)(J - M + 2)}|J + 1, M - 1\rangle, \\
\hat{J}_3^{(+)}|J, M\rangle &= \sqrt{(J + M + 1)(J - M + 1)}|J + 1, M\rangle, \\
\hat{J}_3^{(-)}|J, M\rangle &= -\sqrt{(J + M)(J + M - 1)}|J - 1, M + 1\rangle, \\
\hat{J}_3^{(-)}|J, M\rangle &= -\sqrt{(J - M)(J - M + 1)}|J - 1, M - 1\rangle, \\
\end{align*}
\]

where \( \hat{J}_i^{(+)}, \hat{J}_i^{(-)} = \hat{J}_i^{(+)}, \hat{J}_i^{(-)} = \hat{J}_i^{(-)} \pm i\hat{J}_i^{(-)} \). From these relations one can easily prove the validity of the following relations which will be widely used below:

\[
\begin{align*}
(\hat{J} \times \hat{J}^{(+)}) &= i(\hat{J} + 1)\hat{J}^{(+)}, \quad (\hat{J}^{(+) \times} \hat{J}) = -i\hat{J}^{(+) \dagger} \hat{J}, \\
(\hat{J} \times \hat{J}^{(-)}) &= -i(\hat{J} \hat{J}^{(-)}, \quad (\hat{J}^{(-) \times} \hat{J}) = i\hat{J}^{(-)} \hat{J}^{(+) \dagger} + 1), \\
(\hat{J}^{(+)} \hat{J}^{(-)}) &= \hat{J}(2\hat{J} - 1), \quad (\hat{J}^{(-)} \hat{J}^{(+)}) = (\hat{J} + 1)(2\hat{J} + 3), \\
(\hat{J}^{(+)} \hat{J}^{(-)}) &= i(2\hat{J} - 1)\hat{J}, \quad (\hat{J}^{(-)} \hat{J}^{(+)}) = -i(2\hat{J} + 3)\hat{J};
\end{align*}
\]

\[
\begin{align*}
\hat{J}_i^{(+)} \hat{J}_j^{(-)} &= \hat{J}_i^{(+)} \hat{J}_j^{(-)} = \hat{J}_i^{(+)} \hat{J}_j^{(-)} \hat{J}_k - \hat{J}_k \hat{J}_j; \\
\hat{J}_3^{(-)} \hat{J}_3^{(+) \dagger} &= (\hat{J} + 1)^2 \delta_{ij} - i(\hat{J} + 1)\epsilon_{ijk} \hat{J}_k - \hat{J}_i \hat{J}_j; \\
(\hat{J}^{(+)} \hat{J}^{(+) \dagger}) &= (\hat{J}^{(-)} \hat{J}^{(-)}) = (\hat{J} \hat{J}^{(+) \dagger}) = (\hat{J} \hat{J}^{(-)}) = 0.
\end{align*}
\]

The last line in (3.3) has very clear physical meaning. It states that no scalar operator, which acts only in the space of molecular rotation states, can generate transitions with \( \Delta J \neq 0 \).
4 Mixing intramolecular interaction

For simplicity the model molecular dynamics we are going to consider consists of free molecular rotation with a nuclear spin-mixing interaction imposed on. Vibrational and electron degrees of freedom are not of interest and the vibrational state is assumed to be symmetric.

Let us specify the form of the spin-mixing Hamiltonian $\hat{H}_{\text{mix}}$. Because of Pauli principle, ortho-hydrogen ($I = 1$) can have only odd rotational angular momentum values $J$, whereas para-hydrogen ($I = 0$) must be in a rotational state with even $J$. There must be operators in $\hat{H}_{\text{mix}}$, which generate transitions between ortho- and para-states. $\hat{I}^{(\pm)}$ from Sec.2 are the only operators of such a kind. Because of (2.4), the components of these operators may be contained in $\hat{H}_{\text{mix}}$ in the first degree only. The mentioned correlation between $I$ and $J$ should not be violated by $\hat{H}_{\text{mix}}$. This makes $\hat{I}^{(\pm)}$ be multiplied by vector operators affecting the molecular rotation by changing $J$ by an odd number. We note that any vector operator, which changes $J$ by 3 or more, must inevitably contain the scalar products $(\hat{J}^{(+)} \cdot \hat{J}^{(-)})$ or $(\hat{J}^{(-)} \cdot \hat{J}^{(+)})$ and should be equal to zero in accordance with (3.3). Hence $\hat{J}^{(\pm)}$ are the only operators which $\hat{I}^{(\pm)}$ may be multiplied by. One can now write the general form of the mixing Hamiltonian:

$$\hat{H}_{\text{mix}} = \omega_+(\hat{J}) (\hat{J}^{(+)} \cdot \hat{I}^{(+)}) + (\hat{J}^{(-)} \cdot \hat{I}^{(-)}) \tilde{\omega}_+(\hat{J}) + \omega_-(\hat{J}) (\hat{J}^{(+)} \cdot \hat{I}^{(-)}) + (\hat{J}^{(-)} \cdot \hat{I}^{(+)}) \tilde{\omega}_-(\hat{J}).$$

(4.1)

The scale factors $\omega_\pm(\hat{J})$ in (4.1) account for $J$-dependence of nuclear spin-mixing and can be specified by a microscopic model of mixing interaction. The line over the symbols stands for complex conjugation. Taken with the rotational Hamiltonian $\hat{H}_0 = \omega_0 \hat{J}(\hat{J} + 1)$, the terms (4.1) add up to the total molecular Hamiltonian $\hat{H}$ which will be used below.

5 Heisenberg operator for nuclear spin value $\hat{I}(t)$

Written in the superoperator form, the kinetic equation for the molecules’ density matrix reads

$$\partial_t \hat{\rho}(t) = \mathcal{L}[\hat{\rho}(t)] \equiv \mathcal{L}_0[\hat{\rho}(t)] + \sum_{n=1}^N \nu_n \mathcal{L}_n[\hat{\rho}(t)],$$

(5.1)

where two types of superoperators (Liouvillians) occur: $\mathcal{L}_0[\hat{\rho}(t)] \equiv -i[\hat{H}, \hat{\rho}(t)]$ is the Liouvillian of the free Hamiltonian dynamics; $\mathcal{L}_n$ are the generators of ”irreversible parts” of evolution caused by the environment. Various dissipative generators contribute additively and are specified by the number $n = 1, 2, \ldots, N$; $\nu_n$ give the rates of corresponding dissipative processes. In the present work we are going to describe three types of dissipative Liouvillians and consider the simplest two ones more or less comprehensively.

In the context of the simplest approach, one assumes that any collision with the environment’s particles projects the hydrogen molecule onto pure ortho- and para-states; and this is the only result of the collision in the considered model. Hence

$$\mathcal{L}_1[\hat{\rho}] = \hat{I} \hat{\rho} \hat{I} + (1 - \hat{I}) \hat{\rho} (1 - \hat{I}) - \hat{\rho} \equiv [\hat{I}, [\hat{\rho}, \hat{I}]]$$

(5.2)
One can easily prove that \( \mathcal{L}_1 \) causes the extinction of ortho-para-states coherence induced by the mixing Hamiltonian.

In contrast to the first model, the second one is formulated in terms of molecular frame operators. It postulates that collisions with the environment’s particles cause frequent infinitesimal rotations of \( \mathbf{J} \) (but do not affect directly the nuclear spin):

\[
\mathcal{L}_2[\hat{\rho}] = \hat{J}\hat{\rho}\hat{J} - \frac{1}{2}\hat{J}(\hat{J} + 1)\hat{\rho} - \frac{1}{2}\hat{\rho}\hat{J}(\hat{J} + 1) \quad (5.3)
\]

Note that the ortho-para-states coherence means at the same time the coherence between states with various \( J \) (due to the mentioned \( I - J \) correlation). Because of the last two terms in (5.3) the deorientational collisions destruct the coherence.

The third dissipative model accounts for collisional transitions changing \( J \). In every collision one has \( J \to J \pm 2 \). So the collisions do not initiate direct transitions between ortho- and para-states. The corresponding Liouvillian has the form

\[
\mathcal{L}_3[\hat{\rho}] = [\hat{J}_i^{(-)} q(\hat{J}) \exp\{\beta(2\hat{J} - 1)\} \hat{\rho}_i q(\hat{J}) \hat{J}_i^{(+)}] + [q(\hat{J}) \exp\{-\beta(2\hat{J} - 1)\} \hat{J}_i^{(+)} \hat{\rho}_i \hat{J}_i^{(-)} q(\hat{J})] + H.c., \quad (5.4)
\]

where \( \hat{J}_i^{(\pm)} \equiv \hat{J}_i^{(\pm)} \hat{J}_i^{(\pm)} \) are traceless symmetric tensors; \( \beta = h\omega_0/k_B T \); \( q(\hat{J}) \) is a function of \( \hat{J} \). This model is a straight analog of that one from the work [9]. The conversion induced by (5.5) will be considered in details elsewhere.

Arming with \( \mathcal{L}_1 \) and \( \mathcal{L}_2 \), we may return to Eq.(5.1). It is more convenient to deal with Heisenberg observable \( \hat{O}(t) \) rather than with \( \hat{\rho}(t) \). The corresponding equation of motion for \( \hat{O}(t) \) reads

\[
\partial_t \hat{O}(t) = \mathcal{L}_1[\hat{O}(t)], \quad (5.5)
\]

where the adjoint Liouvillian is introduced. It is determined with respect to the trace scalar product \( Tr(\hat{O}\mathcal{L}[\hat{\rho}]) = Tr(\mathcal{L}^\dagger[\hat{O}]\hat{\rho}) \). Note that \( \mathcal{L}_0^\dagger = -\mathcal{L}_0 \), \( \mathcal{L}_1^\dagger = \mathcal{L}_1 \), and \( \mathcal{L}_2^\dagger = \mathcal{L}_2 \).

Of concern to us is the Heisenberg operator \( \hat{I}(t) \) of the nuclear spin value. The detailed analysis shows that \( \hat{I}(t) \) (as well as any scalar Heisenberg operator) has the following structure:

\[
\hat{I}(t) = A(\hat{J}, t) + B(\hat{J}, t)\hat{I} + C(\hat{J}, t)(\hat{J}^+ \cdot \hat{I}^+) + D(\hat{J}, t)(\hat{J}^+ \cdot \hat{I}^-) + E(\hat{J}, t)\hat{P}_i \hat{J}_j + F(\hat{J}, t)\hat{P}_i \hat{J}_j^+ + \hat{J}_i^+ \hat{P}_i \hat{J}_j^- \quad (5.6)
\]

The coefficients \( A(\hat{J}, t), \ldots, F(\hat{J}, t) \) are to be determined.

With the formal solution of Eq.(5.5) presented as the Taylor expansion

\[
\hat{O}(t) = \sum_{n=0}^{\infty} \frac{t^n}{n!}(\mathcal{L}^\dagger)^n[\hat{O}], \quad (5.7)
\]

one may associate the expansions

\[
A(\hat{J}, t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} A_n(\hat{J}), \ldots, F(\hat{J}, t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} F_n(\hat{J}). \quad (5.8)
\]
After rather cumbersome calculations with the use of algebraic relations from Secs. 2 and 3, we arrive at the following set of iterative equations:

\[ A_{n+1}(J) = -4(J + 1)(2J + 3)L_n^{(+)}(J + 1) + 4J(2J - 1)L_n^{(-)}(J); \quad (5.9) \]

\[ B_{n+1}(J) = \frac{4}{3}J(2J - 1)[L_n^{(+)}(J) - 3L_n^{(-)}(J)] - \frac{4}{3}(J + 1)(2J + 3)[L_n^{(-)}(J + 1) - 3L_n^{(+)}(J + 1)]; \quad (5.10) \]

\[ C_{n+1}^{(+)}(J) = -\frac{i}{6}(J + 1)(2J + 3)J_{+}(J)E_n(J) + i(J - 1)(2J - 3)\bar{\omega}_-(J - 1)F_n(J) \]

\[ + i\omega_+(J)[A_n(J - 1) - A_n(J)] - i\omega_+(J)B_n(J) + [2i\omega_0J - \nu_1 - \nu_2]C_n^{(+)}(J) + i\omega_+(J)(J + 1)D_n(J); \quad (5.11) \]

\[ C_{n+1}^{(-)}(J) = \frac{i}{6}(J + 1)(2J + 3)\omega_-(J)E_n(J - 1) - i(J + 1)(2J + 3)\bar{\omega}_+(J + 1)F_n(J + 1) \]

\[ - i\omega_-(J)[A_n(J - 1) - A_n(J)] + i\omega_-(J)B_n(J) + [2i\omega_0J - \nu_1 - \nu_2]C_n^{(-)}(J) + i\omega_-(J)(J - 1)D_n(J); \quad (5.12) \]

\[ D_{n+1}(J) = -2(2J - 1)L_n^{(+)}(J) - 2(2J + 3)L_n^{(-)}(J + 1) - \nu_2D_n(J); \quad (5.13) \]

\[ E_{n+1}(J) = 4L_n^{(+)}(J) - 4L_n^{(-)}(J + 1) - 3\nu_2E_n(J); \quad (5.14) \]

\[ F_{n+1}(J) = [2i(2J - 1)\omega_0 - 3\nu_2]F_n(J) + 4i\omega_-(J - 1)C_n^{(+)}(J) - 4i\omega_+(J)C_n^{(-)}(J - 1), \quad (5.15) \]

where the combinations

\[ L_n^{(+)}(J) = -i\bar{\omega}_+(J)C_n^{(+)}(J) + i\omega_+(J)\bar{C}_n^{(+)}(J) \]

and

\[ L_n^{(-)}(J) = -i\bar{\omega}_-(J)C_n^{(-)}(J) + i\omega_-(J)\bar{C}_n^{(-)}(J) \]

are introduced. In the case of \( \hat{I}(t) \) we must use the initial conditions when all coefficients \( A_0(J), \ldots, F_0(J) \) are zero except \( B_0(J) = 1 \). In principle, Eqs. (5.9-5.15) let one evaluate \( \hat{I}(t) \) provided the Taylor expansions converge.
6 Conclusion

Fundamentally, the Heisenberg operator $\hat{I}(t)$ let one evaluate any nuclear-spin-dependent magnitude. For example, the expression

$$\langle I(t) \rangle = Tr \hat{I}(t) \hat{\rho}$$

(6.1)
gives the conversion process in an initially prepared non-equilibrium state, where $\hat{\rho}$ is the initial density matrix. One can easily show that (due to the I-J correlations) any relevant $\hat{\rho}$ must obey the equality

$$\left(2\hat{I} + (-1)^J\right) \hat{\rho} = \hat{\rho} = \hat{\rho} \left(2\hat{I} + (-1)^J\right)$$

(6.2)
The stationary density matrix annihilates both the left- and right-hand sides of (6.1). It has a form akin to (5.6) with $t$-independent coefficients. The simplest acceptable (but not stationary) isotropic density matrix is

$$\hat{\rho} = \rho_0(\hat{J}) + \rho_1(\hat{J}) \hat{I}$$

(6.3)
where in accordance with (6.2) $\rho_0(J) = 0$ for odd $J$ and $\rho_0(J) = -\rho_1(J)$ for even $J$.

The proposed model allows rather extended analytical evaluations. Numerical calculations are still inevitable. For this one should specify the factors $\omega_\pm(\hat{J})$ in (4.1). This is an independent problem. There can be faced a situation of bad convergency of the Taylor expansions (5.9) for some $\omega_\pm(\hat{J})$. The analysis of these and related problems will be done elsewhere. As a result we will be able to estimate the value of the model completely.

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