PRODUCTION OF BOSONIC MOLECULES IN THE NONEQUILIBRIUM DYNAMICS OF A DEGENERATE FERMI GAS ACROSS A FESHBACH RESONANCE

A Thesis

by

BOGDAN E. DOBRESCU

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ABSTRACT

Production of Bosonic Molecules in the Nonequilibrium Dynamics of a
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In this thesis I present a nonequilibrium quantum field theory that describes the
production of molecular dimers from a two-component quantum-degenerate atomic
Fermi gas, via a linear downward sweep of a magnetic field across an s-wave Feshbach
resonance. This problem raises interest because it is presently unclear as to why
deviations from the universal Landau-Zener formula for the transition probability at
two-level crossing are observed in the experimentally measured production efficiencies.

The approach is based on evaluating real-time Green functions within the Keldysh-
Schwinger formalism. The effects of quantum statistics associated with Pauli blocking
for fermions and induced emission for bosons, characteristic of particle scattering in
a quantum-degenerate many-body medium, are fully accounted for. I show that the
molecular conversion efficiency is represented by a power series in terms of a dimen-
sionless parameter which, in the zero-temperature limit, depends solely on the initial
gas density and the Landau-Zener parameter. This result reveals a hindrance of the
canonical Landau-Zener transition probability due to many-body effects, and presents
an explanation for the experimentally observed deviations.

A second topic treated in this thesis concerns the study of non-adiabatic tran-
sitions in N-state Landau-Zener systems. In connection to this, I provide a proof of
the conjecture put forth by Brundobler and Elser, regarding the survival probability
on the diabatic levels with maximum/minimum slope.

To my mother

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CHAPTER I

INTRODUCTION

The advances of last years in the experimental techniques of atomic and molec-
ular trapping and cooling, combined with the possibility of externally tuning the
inter-atomic interactions, have ushered in a series of novel applications: the study of
Bose-Einstein condensates (BEC) in the regime of negative scattering length corre-
sponding to attractive interactions and the collapse of the condensate [1, 2, 3, 4, 5], the
formation and propagation of matter-wave soliton trains in a quasi one-dimensional
BEC [6, 7], the first experimental realization of a Fermi degenerate regime in a gas
of alkali atoms [8], the production of Feshbach molecules from BEC and ultracold
thermal samples of bosonic atoms [9, 10, 11, 12, 13, 14, 15, 21] and from quantum
degenerate Fermi gases [16, 17, 18, 19, 20, 21], the emergence of a molecular BEC
from a Fermi gas [22, 23, 24], observation of coherent oscillations between an atomic
condensate and molecules [9, 11, 25], and the examination of Cooper pairing in the
BCS-BEC crossover regime [26, 27, 28, 29, 30].

At the heart of these experiments lies the unprecedented control of the magnitude
and sign of the atomic scattering length in ultracold gases via Feshbach resonances
(FR), which represent an enhancement in the scattering amplitude that appears in
coupled-channel scattering when the energy of two colliding particles in the incoming
open channel is close to the energy of a bound state in a closed channel. To first order
in the coupling between open and closed channels, the scattering is unaltered since, by
definition, there are no continuum states in the closed channel. However, second and
higher order processes are possible in which the two free particles in an open channel

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can scatter, via the coupling between the channels, into an intermediate quasi-bound state in a closed channel, which subsequently decays to give two particles in one of the open channels; they can further scatter back in a quasi-bound state of the same or another closed channel, which subsequently decays, and so on. Direct transitions between two intermediate quasi-bound states of two closed channels are also possible if there is coupling between these channels. All these possible quantum paths connecting two given in and out scattering states have each a corresponding probability amplitude which will contribute additively to the total probability amplitude of the process, and their interference will ultimately determine the transition probability.

In the realm of ultracold alkali gases specific of the experiments enumerated above, the spatial electronic degrees of freedom are virtually frozen. In their electronic ground states, alkali atoms have several different hyperfine states arising from the interaction between their electronic and nuclear spins. Interatomic interactions give rise to transitions between these states and the scattering becomes a multi-channel problem. If a closed channel can support a bound molecular state with a different spin arrangement than that of the two free atoms in the incoming open channel, then the energy difference between the bound state and the two-atom continuum threshold can be experimentally tuned via the Zeeman coupling between the atomic and molecular spins and an externally applied magnetic field.

This simple idea has far reaching consequences, since in a coupled-channel FR-scattering the magnitude and sign of the scattering length are very sensitive to the magnitude and sign of the energy difference between the closed-channel bound state and the open-channel scattering state. Therefore, it has for the first time become possible to experimentally adjust both the sign and magnitude of the effective atom-atom interaction to virtually any desired value! A variable interaction strength is a very exotic degree of freedom in a many-body system, and, adding to the benefits, the

systems for which this is achievable can be very dilute (so that the interparticle separation is very large compared to the characteristic scale of atomic interactions given by magnitude of the corresponding scattering length), and cooled to temperatures at which quantum degeneracy sets in (i.e. the de Broglie wavelength of the particles becomes comparable to the average distance between them). Since the simultaneous interaction between three or more particles is extremely rare in dilute systems, these experiments pertain to a description based only on effective two-body interactions (of variable sign and strength), and many theories and speculative ideas from virtually all areas of physics, developed for various coupling-strength regimes, can be finally tested.

Building on the pioneering theoretical work on FR in alkali gases by Stwalley [31] and Tiesinga *et al.* [32], the first experimental observation of low-energy FR was realized in a dilute BEC of ^{23}Na by Ketterle's group at MIT [33]. This was followed by the observation of FR in other alkalis, both bosonic [34, 35, 36, 37] and fermionic [38, 39, 40, 41, 42, 43].

The many fascinating experiments mentioned in the beginning, all based on FR, soon emerged. In the studies of the BEC collapse, the scattering length of the atoms in the condensate is tuned to negative values of different magnitudes, corresponding to attractive interactions. When the potential energy of these attractive interactions overcomes the stabilizing kinetic energy the collapse of the BEC occurs, resulting in the expulsion of a large fraction of atoms from the condensate.

In a different setting, a quasi one-dimensional BEC, initially tuned to a positive scattering length (SCL) near a FR, is abruptly taken to the other side of the resonance which corresponds to a negative SCL. The low dimensionality of the system enhances the phase fluctuations, and the collapse of BEC is prevented by the formation of a train of solitons that repel each other.

In the experiments which resulted in the observation of coherent oscillations between an atomic condensate and molecules, the off-resonant SCL was compensated by tuning the resonant part of SCL to an equal and opposite value, such that, initially, the effective interaction in an atomic BEC was virtually zero. This non-interacting BEC was subsequently subjected to a trapezoidal pulse in the magnetic field directed towards the resonance, and oscillations in the number of atoms, due to the partial conversion of a fraction of them into molecules, were observed as a function of the duration of the pulse.

Experiments designed towards the production of a large number of molecular dimers from ultracold thermal and BEC samples of bosonic atoms, as well as from quantum-degenerate two-component atomic Fermi gases soon followed. The technique used for this purpose was a linear downward sweeping of a magnetic field across a FR. The atomic sample, prepared as an incoherent mixture of two equally populated hyperfine states, has initially a negative SCL, corresponding to an effective attractive interaction between the atoms. The strength of the inter-atomic interaction is then steadily increased by applying a linearly variable magnetic field that drives the system towards the FR. As a result, the atoms tend to form quasi-bound molecular states whose life-time increases as the resonance is approached. However, as previously mentioned, these quasi-bound states belong to a closed channel and hence are only metastable as long as the magnetic field is above the resonance. Only when the field reaches the region below the resonance, corresponding to a positive SCL, do these quasi-bound states turn into truly stable molecules. The molecular conversion efficiency (MCE) is the result of a subtle interplay between sweeping rate, resonance width, temperature, density and statistics.

The MCE in the bosonic case can be reasonably well described within a mean-field approximation (see [44, 45] and references therein) that reduces the many-body

physics to a two-state Landau-Zener (LZ) system [46, 47, 48, 49].

In contrast, the Fermi case requires, at the very least, the inclusion of all possible single-particle states that can be occupied by the fermionic atoms, and the effects of statistics need to be manifestly included in the dynamics of the molecular production, as these gases are in a quantum-degenerate regime. This is the main subject investigated in this thesis.

With this scope in mind, the thesis is organized as follows. In Chapter II, after a short review of nonadiabatic transitions in N-state Landau-Zener systems, I provide a proof for the Brundobler-Elser conjecture [50] regarding the survival probability on the diabatic levels with maximum/minimum slope. In this proof, I reveal the connection between the Brundobler-Elser formula for a general N-state Landau-Zener system and the exactly solvable bow-tie model. The special importance of the diabatic levels with an extreme slope is emphasized throughout.

Chapter III is dedicated to the analysis of atom-molecule conversion in ultra-degenerate two-component Fermi gases subject to a linear downward sweep of a magnetic field across an s-wave FR, in the spirit of experiments [16, 17, 18, 21]. In connection to this, I present a nonequilibrium quantum field theory based on evaluating real-time Green functions within the Keldysh-Schwinger formalism. The effects of quantum statistics associated with Pauli blocking for fermions and induced emission for bosons, characteristic of particle scattering in a quantum-degenerate many-body medium, are fully accounted for. I show that the molecular conversion efficiency is represented by a power series in terms of a dimensionless parameter which, in the zero-temperature limit, depends solely on the initial gas density and the Landau-Zener parameter. This result reveals a hindrance of the canonical Landau-Zener transition probability due to many-body effects, and presents an explanation for the experimentally observed deviations [16, 17, 18, 21].

Along the way, I contrast this theory and its results with previously proposed semi-phenomenological scenarios [51, 52] and numerical calculations [53, 54, 55]. A summary and concluding remarks are provided in Chapter IV.

CHAPTER II

NONADIABATIC TRANSITIONS AND LANDAU-ZENER DYNAMICS

The study of nonadiabatic transitions (NAT) in the region of diabatic potential energy curve crossing is of fundamental importance in a wide variety of fields from physics, chemistry [56, 57, 58] and biophysics [59, 60]. In physics, the problem is ubiquitous, ranging from high energy physics (e.g., elementary-particle production in strong external fields [61] and the solar-neutrino puzzle [62]) to condensed matter and mesoscopic physics (e.g., atoms scattering off surfaces [63], nuclear magnetic resonance [64], charge transport in nanostructures [65, 66, 67, 68, 69, 70, 71], quantum computing [72, 73], spin transitions, relaxation and hysteresis in nanomagnets [74, 75, 76, 77, 78], Bose-Einstein condensates [79, 80, 81, 82, 83, 84], production of Feshbach molecules from quantum degenerate Fermi gases [16, 17, 18, 19, 21, 20, 22, 23, 24]), and atomic physics (e.g., atomic collisions [46, 47, 85, 86, 87], behavior of atoms in laser fields [57, 88]).

The paradigm for the NAT is the famous two-state Landau-Zener (LZ) model [46, 47, 48, 49] that dates back to 1932. The next section is a short review of its solution. Section B is devoted to its N-level generalization and concludes with the proof of the Brundobler-Elser conjecture.

A. 2-level Landau-Zener System

The Hamiltonian of this model reads $\hat{H}(t) = \hat{H}_0(t) + \hat{V}$, with

$$\hat{H}_0(t) = \sum_{j=1,2} (\varepsilon_j + \beta_j t)\,|j\rangle\,\langle j| \quad \text{and} \quad \hat{V} = V\,|1\rangle\,\langle 2| + \text{h.c.}, \tag{2.1}$$

where h.c. stands for hermitian conjugation. Eq.(2.1) can be regarded as a linear approximation of a general time-dependent two-state Hamiltonian

$$\hat{H}_{gen}\left(t\right) = \sum_{j=1,2} \mathcal{E}_j\left(t\right) \left|j\right\rangle \left\langle j\right| + \left[V\left(t\right)\left|1\right\rangle\left\langle 2\right| + \text{h.c.}\right] \tag{2.2}$$

in the vicinity of a point of crossing, t_c, of the two energy curves $\mathcal{E}_1\left(t\right)$ and $\mathcal{E}_2\left(t\right)$ (i.e., $\mathcal{E}_1\left(t_c\right) = \mathcal{E}_2\left(t_c\right)$).

The two ket vectors $\left|1\right\rangle$ and $\left|2\right\rangle$ of Eq.(2.1) describe the so-called diabatic states whose time-dependent energies, referred to as diabatic energy curves, are slanted straight lines with slopes β_j. As the system approaches the crossing, transitions between the two diabatic states, mediated by the interaction $\hat{V}$, can occur. The dynamics of the system is a result of the interplay between the strength of the coupling $\left|V\right|$ and the rate at which the system is driven through the crossing region, determined by $\left|\beta_1 - \beta_2\right|$. The characteristic time of transition is of the order of $\tau_{LZ} \approx \frac{|V|}{|\beta_1 - \beta_2|}$, whereas the characteristic time scale for the stationary internal dynamics (i.e., in the absence of external perturbations) of the system at crossing is of the order of $\tau_{char} \approx \frac{\hbar}{|V|}$. Therefore, when $\tau_{LZ} \gg \tau_{char}$ the evolution of the system is adiabatic, and the description of this case is most suitably given in terms of adiabatic states $\left|\Psi_k\left(t\right)\right\rangle$, and the corresponding adiabatic energy curves $E_k\left(t\right)$, which are the solutions of the eigenvalue problem for the Hamiltonian $\hat{H}\left(t\right)$ at each instant t,

$$\hat{H}\left(t\right)\left|\Psi_k\left(t\right)\right\rangle = E_k\left(t\right)\left|\Psi_k\left(t\right)\right\rangle. \tag{2.3}$$

The crossing of the diabatic energy curves corresponds to an avoided crossing of the adiabatic energy curves, with a splitting proportional to the strength of the coupling $\left|V\right|$. The adiabatic condition $\left\langle\dot{\Psi}_k\left(t\right)|\Psi_k\left(t\right)\right\rangle = 0$ allows to fix the time-dependent phases of the diabatic states [89], and in the large time limit, $\left|t\right| \to \infty$,

the adiabatic energy curves will asymptotically approach the diabatic ones. This behavior is summarized in Fig.1.
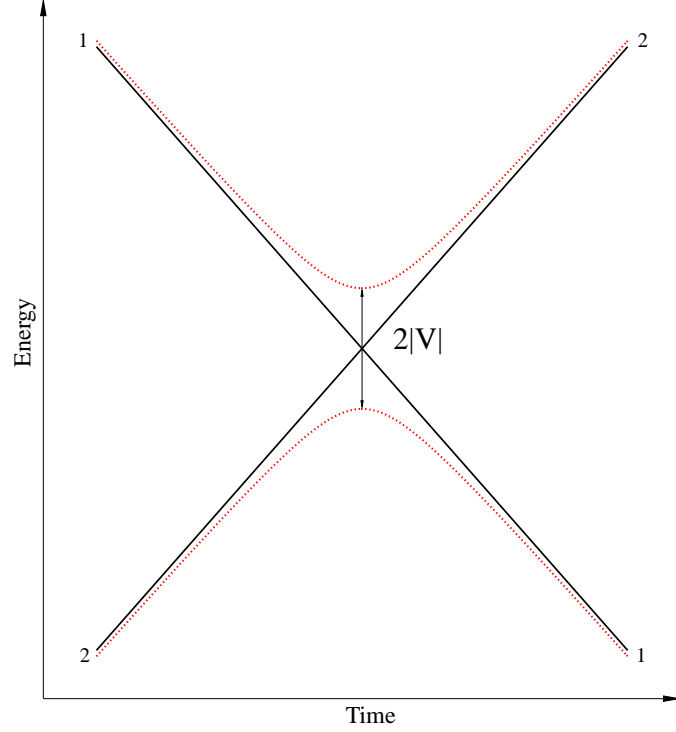
Fig. 1. Adiabatic (dotted lines) and diabatic (continuous lines) energy curves for a two-level Landau-Zener system, with a coupling strength $|V|$.

The problem of calculating the transition probability between the diabatic states requires the evaluation of the matrix elements of the time evolution operator, $\hat{U}(t, t_0)$, in the basis provided by these states. The formal solution of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \hat{U}(t, t_0)}{\partial t} = \hat{H}(t) \hat{U}(t, t_0), \tag{2.4}$$

subject to the initial condition $\hat{U}(t_0, t_0) = \hat{\mathbf{1}}$, reads

$$
\begin{aligned}
\hat{U}(t, t_0) = {} & \hat{U}_0(t, t_0) + \sum_{n=1}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \\
& \times \hat{U}_0(t, \tau_n) \hat{V} \hat{U}_0(\tau_n, \tau_{n-1}) \hat{V} \cdots \hat{U}_0(\tau_2, \tau_1) \hat{V} \hat{U}_0(\tau_1, t_0),
\end{aligned} \tag{2.5}
$$

where

$$\hat{U}_0\left(\tau_k, \tau_j\right) = \exp\left[\frac{1}{i\hbar}\int_{\tau_j}^{\tau_k}\hat{H}_0\left(\tau\right)d\tau\right] \tag{2.6}$$

is the free time-evolution operator corresponding to $\hat{H}_0$.

From Eqs. (2.1) and (2.6) it follows that

$$\langle\alpha|\hat{U}_0\left(\tau_k, \tau_j\right)|\beta\rangle = \delta\left(\alpha, \beta\right)\exp\left\{\left(\frac{1}{i\hbar}\right)\left[\varepsilon_\alpha\left(\tau_k - \tau_j\right) + \frac{\beta_\alpha}{2}\left(\tau_k^2 - \tau_j^2\right)\right]\right\} \tag{2.7}$$

for $\alpha, \beta = 1, 2$, with $\delta\left(\alpha, \beta\right)$ being the Kronecker delta. Therefore, $\left|\langle 1|\hat{U}\left(+\infty, -\infty\right)|1\rangle\right| = |S_{11}|$, where

$$S_{11} = 1 + \sum_{n=1}^{\infty}\left(\frac{|V|}{i\hbar}\right)^{2n}C_{2n} \tag{2.8}$$

and

$$
\begin{aligned}
C_{2n} &= \int_{-\infty}^{+\infty}d\tau_{2n}\int_{-\infty}^{\tau_{2n}}d\tau_{2n-1}\cdots\int_{-\infty}^{\tau_2}d\tau_1 \\
&\times\exp\left\{\frac{\left(\beta_2 - \beta_1\right)}{2i\hbar}\left[\left(\tau_{2n}^2 - \tau_{2n-1}^2\right) + \cdots + \left(\tau_4^2 - \tau_3^2\right) + \left(\tau_2^2 - \tau_1^2\right)\right]\right\} \\
&\times\exp\left\{\frac{\left(\varepsilon_2 - \varepsilon_1\right)}{i\hbar}\left[\left(\tau_{2n} - \tau_{2n-1}\right) + \cdots + \left(\tau_4 - \tau_3\right) + \left(\tau_2 - \tau_1\right)\right]\right\}. \tag{2.9}
\end{aligned}
$$

The integrals C_{2n} can be evaluated by introducing the following change of variables proposed by Kayanuma and Fukuchi in [90]:

$$
\begin{aligned}
\tau_1 &= x_1 \in \left(-\infty, +\infty\right), \\
\tau_{2k} &= \tau_{2k-1} + y_k, \quad y_k \in \left[0, +\infty\right), \quad \text{for any } k = 1, 2, \ldots, n, \\
\tau_{2k-1} &= \tau_{2k-2} + \left(x_k - x_{k-1}\right), \quad x_k \in \left[x_{k-1}, +\infty\right), \quad \text{for any } k = 2, 3\ldots, n,
\end{aligned}
$$

where $n = 1, 2, \ldots, \infty$. The Jacobian of this transformation is 1, and Eq.(2.9) becomes

$$
C_{2n} = \int_0^\infty dy_1 \int_0^\infty dy_2 \cdots \int_0^\infty dy_n \, \exp \left\{ \frac{(\varepsilon_2 - \varepsilon_1)}{i\hbar} \left(\sum_{k=1}^n y_k \right) + \frac{(\beta_2 - \beta_1)}{2i\hbar} \left(\sum_{k=1}^n y_k \right)^2 \right\}
$$

$$
\times \int_{-\infty}^\infty dx_1 \int_{x_1}^\infty dx_2 \int_{x_2}^\infty dx_3 \cdots \int_{x_{n-1}}^\infty dx_n \, \exp \left\{ \frac{(\beta_2 - \beta_1)}{i\hbar} \left(\sum_{k=1}^n x_k y_k \right) \right\}. \quad (2.10)
$$

Since the integrand of (2.10) is symmetric with respect to any permutation of pairs of integration variables $(x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)$, the limits of integration for the x-variables can be extended from $-\infty$ to $+\infty$, i.e.

$$
C_{2n} = \frac{1}{n!} \int_0^\infty dy_1 \cdots \int_0^\infty dy_n \, \exp \left\{ \frac{(\varepsilon_2 - \varepsilon_1)}{i\hbar} \left(\sum_{k=1}^n y_k \right) + \frac{(\beta_2 - \beta_1)}{2i\hbar} \left(\sum_{k=1}^n y_k \right)^2 \right\}
$$

$$
\times \int_{-\infty}^\infty dx_1 \cdots \int_{-\infty}^\infty dx_n \, \exp \left\{ \frac{(\beta_2 - \beta_1)}{i\hbar} \left(\sum_{k=1}^n x_k y_k \right) \right\}
$$

$$
= \frac{1}{n!} \int_0^\infty dy_1 \cdots \int_0^\infty dy_n \, \exp \left\{ \frac{(\varepsilon_2 - \varepsilon_1)}{i\hbar} \left(\sum_{k=1}^n y_k \right) + \frac{(\beta_2 - \beta_1)}{2i\hbar} \left(\sum_{k=1}^n y_k \right)^2 \right\}
$$

$$
\times \left(\prod_{k=1}^n \frac{2\pi\hbar}{|\beta_2 - \beta_1|} \delta(y_k) \right) = \frac{1}{n!} \left(\frac{\pi\hbar}{|\beta_2 - \beta_1|} \right)^n, \quad (2.11)
$$

where the integral representation $\frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{\pm ixy} dx = \delta(y)$ of the Dirac delta function was used.

From Eqs. (2.8) and (2.11) one obtains

$$
\left| \langle 1 | \hat{U}(+\infty, -\infty) | 1 \rangle \right| = |S_{11}| = 1 + \sum_{n=1}^\infty \frac{1}{n!} \left(-\pi \frac{|V|^2}{\hbar |\beta_2 - \beta_1|} \right)^n = \exp \left(-\pi \frac{|V|^2}{\hbar |\beta_2 - \beta_1|} \right).
$$

$$
(2.12)
$$

If, at $t_0 = -\infty$, the system is prepared in the state $|1\rangle$, then the famous LZ

transition probabilities at $t = +\infty$ are given by

$$P_{11} = \left| \langle 1| \hat{U} \left(+\infty, -\infty\right) |1\rangle \right|^2 = \exp\left(-2\pi \frac{|V|^2}{\hbar \left|\beta_2 - \beta_1\right|}\right), \qquad (2.13)$$

$$P_{12} = \left| \langle 2| \hat{U} \left(+\infty, -\infty\right) |1\rangle \right|^2 = 1 - P_{11}. \qquad (2.14)$$

The proof outlined above, based on the evaluation of of the whole series expansion of the time evolution operator, is complementary to the original solutions given by Landau [46] in terms of analytic continuation in the complex time domain of the asymptotic solution of the differential equation satisfied by the time-dependent probability amplitudes of the diabatic states for large t, and by Zener [47] by analyzing the large t asymptotics of the Weber functions, which are the exact solutions for these probability amplitudes. The main advantage of this approach resides in its versatility, being readily applicable in multi-level systems, where analytic continuation of an asymptotic solution (when known) usually has to cope with a very intricate Stokes phenomenon.

B.   N-level Landau-Zener System. Proof of the Brundobler-Elser Conjecture.

The generalization of (2.1) to an N-state system reads

$$\hat{H}\left(t\right) = \sum_{k=1}^{N} \left(\varepsilon_k + \beta_k t\right) |k\rangle \langle k| + \sum_{j,k=1}^{N} V_{jk} |j\rangle \langle k|, \qquad (2.15)$$

where $V_{jj} = 0$, and $V_{jk} = V_{kj}^*$. The solution for the transition probabilities, P_{jk}, among the diabatic states is presently known only for some special cases of (2.15), and the general problem is still the object of active research.

The first N-level system analyzed was a spin $s = \left(N-1\right)/2$ in a time-dependent magnetic field [48, 91], and in this case the problem can be reduced exactly to a

two-level one, based on the expression of the elements of any Wigner rotation matrix for a spin s in terms of the elements of the corresponding two-dimensional matrix for a spin $1/2$.

The next special-case model in which one diabatic energy curve crosses and interacts with a band of parallel ones was solved by Demkov and Osherov [92] using a Laplace transformation (see also the recent solution [93] based on a Fourier transformation method).

Building on the work of Brundobler and Elser [50], Ostrovsky and Nakamura [94] have solved the so-called bow-tie model by analyzing the asymptotic form of the exact analytical solutions expressed in terms of contour integrals given in [50]. In this model, all diabatic levels cross simultaneously at the same point, and the coupling is provided only by the interaction of one special level, say of slope β_1, with all the others. For this particular case, the expression of Eq.(2.15) reduces to

$$\hat{H}_{bow-tie}\left(t\right) = \sum_{k=1}^{N} \beta_k t \left|k\right\rangle \left\langle k\right| + \sum_{k=2}^{N} \left(V_{1k} \left|1\right\rangle \left\langle k\right| + \text{h.c.}\right). \qquad (2.16)$$

Demkov and Ostrovsky have subsequently considered a generalized bow-tie model [95] described by the Hamiltonian

$$\hat{H}_{gen-bow-tie}\left(t\right) = \frac{\varepsilon}{2} \left|0^+\right\rangle \left\langle 0^+\right| - \frac{\varepsilon}{2} \left|0^-\right\rangle \left\langle 0^-\right| + \sum_{k=1}^{N} \frac{V_k}{\sqrt{2}} \left(\left|0^+\right\rangle \left\langle k\right| + \left|0^-\right\rangle \left\langle k\right| + \text{h.c.}\right).$$

Whereas the complete solution of the general Hamiltonian (2.15) is still elusive, based on the exactly solvable special cases known at the time and numerical testing, Brundobler and Elser [50] have conjectured the form of the survival probability for the diabatic states corresponding to energy levels of maximal or minimal slope, namely

$$P_{11} = \left|\left\langle 1\right| \hat{U}\left(+\infty, -\infty\right) \left|1\right\rangle\right|^2 = \exp\left(-2\pi \sum_{k=2}^{N} \frac{\left|V_{1k}\right|^2}{\hbar \left|\beta_1 - \beta_k\right|}\right), \qquad (2.17)$$

if $\beta_1 = \max_k \beta_k$ or $\beta_1 = \min_k \beta_k$. After its proposal in 1993, this conjecture was validated by all the special cases solved since then [67, 94, 95]. The physical picture behind (2.17) amounts to an independent crossing approximation in which the system, initially populated in the diabatic state $|1\rangle$, propagates only in the positive direction of time and survives each crossing with a probability equal to that of a canonical 2-level LZ-model.

Following the original approach of Landau, Shytov [96] proposed a proof of the Brundobler-Elser formula (BEF) (2.17) based on the analytic continuation in the complex time domain of the asymptotic solution for large t. While the arguments presented are pertinent, a rigorous analysis of the Stokes phenomenon is missing, the author simply assuming (without proof) that when matching the asymptotic expansions of the exact wave function many of its components corresponding to the probability amplitudes of diabatic states have a vanishing contribution.

Volkov and Ostrovsky [97] have attempted a proof of the BEF based on time-dependent perturbation theory, but their arguments are erroneous.

Dobrescu and Sinitsyn [98] have subsequently revealed the shortcomings of [97] and proved the BEF by reducing the general problem to the special case of the bow-tie model. This proof is presented below.

From Eqs. (2.5), (2.6), (2.7) and (2.15) it follows that $\left| \langle 1 | \hat{U} (+\infty, -\infty) | 1 \rangle \right| = |S_{11}|$, where

$$S_{11} = 1 + \sum_{n=2}^{\infty} \left(\frac{1}{i\hbar} \right)^n \sum_{k_1=1}^{N} \sum_{k_2=1}^{N} \cdots \sum_{k_{n-1}=1}^{N} \left(V_{1k_{n-1}} V_{k_{n-1}k_{n-2}} \cdots V_{k_2 k_1} V_{k_1 1} \right) C_n \left(k_1, \ldots, k_{n-1} \right),$$

(2.18)

and

$$
\begin{aligned}
C_n\left(k_1, \ldots, k_{n-1}\right) \;=\; & \int_{-\infty}^{+\infty} d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} d\tau_1 \\
& \times \exp\left[\left(\frac{1}{i\hbar}\right) \varepsilon_{k_1}\left(\tau_2 - \tau_1\right) + \left(\frac{1}{i\hbar}\right)\frac{\beta_{k_1}}{2}\left(\tau_2^2 - \tau_1^2\right)\right] \\
& \times \exp\left[\left(\frac{1}{i\hbar}\right) \varepsilon_{k_2}\left(\tau_3 - \tau_2\right) + \left(\frac{1}{i\hbar}\right)\frac{\beta_{k_2}}{2}\left(\tau_3^2 - \tau_2^2\right)\right] \\
& \quad\vdots \\
& \times \exp\left[\left(\frac{1}{i\hbar}\right) \varepsilon_{k_{n-1}}\left(\tau_n - \tau_{n-1}\right) + \left(\frac{1}{i\hbar}\right)\frac{\beta_{k_{n-1}}}{2}\left(\tau_n^2 - \tau_{n-1}^2\right)\right] \\
& \times \exp\left[-\left(\frac{1}{i\hbar}\right) \varepsilon_1\left(\tau_n - \tau_1\right) - \left(\frac{1}{i\hbar}\right)\frac{\beta_1}{2}\left(\tau_n^2 - \tau_1^2\right)\right], \quad (2.19)
\end{aligned}
$$

with $V_{jk} = 0$ for $j = k$.

Upon introducing the change of variables

$$
\begin{aligned}
\tau_1 \;&=\; x_1 \in (-\infty, +\infty), \\
\tau_{j+1} \;&=\; \tau_j + x_{j+1}, \quad x_{j+1} \in [0, +\infty), \quad \text{for any } j = 1, 2, \ldots, (n-1),
\end{aligned}
$$

the integral (2.19) becomes

$$
C_n\left(k_1, \ldots, k_{n-1}\right) = \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dx_2 \cdots \int_0^{\infty} dx_n \; F\left(x_1, \ldots, x_n\right), \quad (2.20)
$$

where

$$
\begin{aligned}
F\left(x_1, \ldots, x_n\right) \;=\; & \exp\left[i x_1 \left\{B\left(k_1\right) x_2 + B\left(k_2\right) x_3 + \cdots + B\left(k_{n-1}\right) x_n\right\}\right] \\
& \times \exp\left[\left(\frac{i}{2}\right)\left\{B\left(k_1\right) x_2^2 + B\left(k_2\right) x_3^2 + \cdots + B\left(k_{n-1}\right) x_n^2\right\}\right] \\
& \times \exp\left[i\left\{B\left(k_2\right)\left(x_3 x_2\right) + \cdots + B\left(k_{n-1}\right)\left(x_n \sum_{l=2}^{n-1} x_l\right)\right\}\right] \\
& \times \exp\left[i\left\{E\left(k_1\right) x_2 + E\left(k_2\right) x_3 + \cdots + E\left(k_{n-1}\right) x_n\right\}\right], \quad (2.21)
\end{aligned}
$$

and

$$E\left(k_j\right) = \frac{\varepsilon_1 - \varepsilon_{k_j}}{\hbar}, \quad \text{and} \quad B\left(k_j\right) = \frac{\beta_1 - \beta_{k_j}}{\hbar}. \tag{2.22}$$

The integrals in (2.20) exist only in the sense of distributions (i.e., generalized functions) and their behavior at $\pm\infty$ needs to be regularized. This amounts to

$$
\begin{aligned}
C_n &= \lim_{\eta\to 0_+} \left\{ \int_{-\infty}^0 dx_1 \int_0^\infty dx_2 \cdots \int_0^\infty dx_n \ F\left(x_1, x_2, \ldots, x_n\right) e^{-\eta(-x_1+x_2+\ldots+x_n)} \right.\\
&\quad \left. + \int_0^\infty dx_1 \int_0^\infty dx_2 \cdots \int_0^\infty dx_n \ F\left(x_1, x_2, \ldots, x_n\right) e^{-\eta(x_1+x_2+\ldots+x_n)} \right\}. \tag{2.23}
\end{aligned}
$$

Upon integrating over x_1 in (2.23) one obtains

$$C_n = \lim_{\eta\to 0_+} J\left(\eta\right), \tag{2.24}$$

where

$$J\left(\eta\right) = \int_0^\infty dx_2 \int_0^\infty dx_3 \cdots \int_0^\infty dx_n \ g\left(x_2, x_3, \ldots, x_n; \eta\right) \exp\left[i\varphi\left(x_2, x_3, \ldots, x_n; \eta\right)\right], \tag{2.25}$$

$$g\left(x_2, x_3, \ldots, x_n; \eta\right) = \frac{2\eta \exp\left[-\eta\left(x_2 + x_3 + \cdots + x_n\right)\right]}{\left[B\left(k_1\right) x_2 + B\left(k_2\right) x_3 + \cdots + B\left(k_{n-1}\right) x_n\right]^2 + \eta^2}, \tag{2.26}$$

$$
\begin{aligned}
\varphi\left(x_2, x_3, \ldots, x_n; \eta\right) &= E\left(k_1\right) x_2 + E\left(k_2\right) x_3 + \cdots + E\left(k_{n-1}\right) x_n \\
&\quad + \frac{1}{2}\left[B\left(k_1\right) x_2^2 + B\left(k_2\right) x_3^2 + \cdots + B\left(k_{n-1}\right) x_n^2\right] \\
&\quad + B\left(k_2\right)\left(x_3 x_2\right) + \cdots + B\left(k_{n-1}\right)\left(x_n \sum_{l=2}^{n-1} x_l\right). \tag{2.27}
\end{aligned}
$$

From Eqs. (2.25), (2.26) and (2.27) it follows that

$$
\begin{aligned}
|J\left(\eta\right)| &\leq \int_0^\infty dx_2 \cdots \int_0^\infty dx_n \ |g\left(x_2, x_3, \ldots, x_n; \eta\right)| \\
&= \int_0^\infty dx_2 \cdots \int_0^\infty dx_n \frac{2\eta \exp\left[-\eta\left(x_2 + \cdots + x_n\right)\right]}{\left[B\left(k_1\right) x_2 + \cdots + B\left(k_{n-1}\right) x_n\right]^2 + \eta^2}. \tag{2.28}
\end{aligned}
$$

The results obtained so far hold for any slope β_1, and the coefficients $B\left(k_j\right)$ are

arbitrary real numbers.

In the following I will specialize to the case when β_1 is a maximal/minimal slope, and analyze the conditions under which the right-hand side of Eq.(2.28) becomes zero. This in turn will provide the quantum paths

$$1 \to k_1 \to k_2 \to \ldots \to k_{n-1} \to 1$$

of order n that can have a nonvanishing contribution to the series (2.18).

If β_1 is an extremum, then all $B(k_j) \geq 0$ (if $\beta_1 = \max_k \beta_k$) or all $B(k_j) \leq 0$ (if $\beta_1 = \min_k \beta_k$). Let ν be the number of coefficients $B(k_j)$ whose value is zero (i.e. for which $k_j = 1$). If $B(k_j) = 0$, then one can integrate over x_{j+1} in (2.28)

$$\int_0^\infty dx_{j+1} \exp\left[-\eta x_{j+1}\right] = \frac{1}{\eta},$$

and, after integrating over all ν variables x_{j+1} whose coefficients $B(k_j) = 0$, one obtains

$$
\begin{aligned}
\lim_{\eta \to 0_+} |J(\eta)| \;\leq\;& \lim_{\eta \to 0_+} \frac{2}{\eta^\nu} \int_0^\infty dy_1 \int_0^\infty dy_2 \cdots \int_0^\infty dy_{n-\nu-1} \\
& \times \frac{\eta \exp\left[-\eta\left(y_1 + y_2 + \cdots + y_{n-\nu-1}\right)\right]}{\left[\widetilde{B}_1 y_1 + \widetilde{B}_2 y_2 + \cdots + \widetilde{B}_{n-\nu-1} y_{n-\nu-1}\right]^2 + \eta^2} \\
=\;& \lim_{\eta \to 0_+} \frac{2}{\eta^\nu} \int_0^\eta dy_1 \int_0^\eta dy_2 \cdots \int_0^\eta dy_{n-\nu-1} \\
& \times \frac{\eta \exp\left[-\eta\left(y_1 + y_2 + \cdots + y_{n-\nu-1}\right)\right]}{\left[\widetilde{B}_1 y_1 + \widetilde{B}_2 y_2 + \cdots + \widetilde{B}_{n-\nu-1} y_{n-\nu-1}\right]^2 + \eta^2}, \qquad (2.29)
\end{aligned}
$$

where the remaining $(n - \nu - 1)$ dummy integration x-variables whose coefficients $B(k_l) \neq 0$ have been renamed y_l, and their corresponding coefficients have been renamed $\widetilde{B}_l$ in order to simplify the notation.

For any continuous function f defined on a compact interval $[a, b]$ the relation

$\int_a^b f(x)\, dx = f(\xi)(b-a)$ holds, for some $\xi \in [a, b]$. Therefore,

$$
\int_0^\eta dy_1 \int_0^\eta dy_2 \cdots \int_0^\eta dy_{n-\nu-1} \frac{\exp\left[-\eta\left(y_1 + y_2 + \cdots + y_{n-\nu-1}\right)\right]}{\left[\widetilde{B}_1 y_1 + \widetilde{B}_2 y_2 + \cdots + \widetilde{B}_{n-\nu-1} y_{n-\nu-1}\right]^2 + \eta^2}
$$

$$
= \eta^{n-\nu-3} \frac{\exp\left[-\eta^2\left(\xi_1 + \xi_2 + \cdots + \xi_{n-\nu-1}\right)\right]}{\left[\widetilde{B}_1 \xi_1 + \widetilde{B}_2 \xi_2 + \cdots + \widetilde{B}_{n-\nu-1} \xi_{n-\nu-1}\right]^2 + 1}, \tag{2.30}
$$

where $\xi_j \in [0, 1]$, for any $j = 1, 2, \ldots, (n - \nu - 1)$.

From Eqs. (2.29) and (2.30) one obtains

$$
\lim_{\eta \to 0_+} |J(\eta)| \le \lim_{\eta \to 0_+} \eta^{n-2\nu-2} \frac{2 \exp\left[-\eta^2\left(\xi_1 + \xi_2 + \cdots + \xi_{n-\nu-1}\right)\right]}{\left[\widetilde{B}_1 \xi_1 + \widetilde{B}_2 \xi_2 + \cdots + \widetilde{B}_{n-\nu-1} \xi_{n-\nu-1}\right]^2 + 1}. \tag{2.31}
$$

Since $C_n = \lim_{\eta \to 0_+} J(\eta)$, from Eq.(2.31) it follows that, at each order n, the only possible non-zero contributions to the series (2.18) can come from quantum paths $1 \to k_1 \to k_2 \to \ldots \to k_{n-1} \to 1$ in which the number ν of intermediate diabatic states with $k_j = 1$ (i.e. for which $B(k_j) = 0$) satisfies the inequality

$$
\nu \ge \frac{n-2}{2}. \tag{2.32}
$$

However, since $V_{jk} = 0$ for $j = k$, the maximum possible number of intermediate states with $k_j = 1$ in a quantum path $1 \to k_1 \to k_2 \to \ldots \to k_{n-1} \to 1$ is $\frac{n-3}{2}$ for odd n, and $\frac{n-2}{2}$ for even n. Therefore, Eq.(2.32) implies that only quantum paths of even order and with the very special structure

$$
1 \to k_1 \to 1 \to k_2 \to 1 \to \ldots \to 1 \to k_{\frac{n}{2}} \to 1,
$$

where $k_l \ne 1$ for any $l = 1, 2, \ldots, \frac{n}{2}$, can have a nonvanishing contribution to the survival probability on the diabatic level 1 of maximal/minimal slope.

Therefore, Eq.(2.18) reduces to

$$
\begin{aligned}
S_{11} &= 1 + \sum_{m=1}^{\infty} \left(\frac{1}{i\hbar}\right)^{2m} \sum_{k_1=2}^{N} \sum_{k_2=2}^{N} \cdots \sum_{k_m=2}^{N} |V_{1k_1}|^2 |V_{1k_2}|^2 \cdots |V_{1k_m}|^2 \\
&\quad \times \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \cdots \int_{-\infty}^{\tau_{2m-1}} d\tau_{2m} \\
&\quad \times \exp\left[i\frac{B(k_1)}{2}\left(\tau_1^2 - \tau_2^2\right) + \cdots + i\frac{B(k_m)}{2}\left(\tau_{2m-1}^2 - \tau_{2m}^2\right)\right] \\
&\quad \times \exp\left[iE(k_1)(\tau_1 - \tau_2) + \cdots + iE(k_m)(\tau_{2m-1} - \tau_{2m})\right]. \quad (2.33)
\end{aligned}
$$

Following a complicated procedure based on the mathematical induction method, Volkov and Ostrovsky [97] have actually only shown that the contribution to the transition probability from the particular class of quantum paths $1 \to k_1 \to k_2 \to \ldots \to k_{n-1} \to 1$ in which all $k_j \neq 1$ is zero (see Eqs. (A.1) through (A.5) of [97]). However, as explicitly proven above, there are many other possible paths with vanishing probability amplitude: all paths $1 \to k_1 \to k_2 \to \ldots \to k_{n-1} \to 1$ in which some of the intermediate diabatic states k_j are equal to 1 have zero contribution if their number of states with $k_j = 1$ is less than $\frac{n-2}{2}$. This large class of possible quantum paths is completely overlooked in [97].

From this point on, Volkov and Ostrovsky [97] no longer use the property of β_1 being maximal/minimal and their proof is obviously erroneous since the BEF holds only for an extreme slope. A detailed account of their mathematical errors is contained in [98].

In the next step I will prove that if β_1 is maximal/minimal, then S_{11} does not depend on $E(l_j)$, for any $l_j = 2, 3, \ldots, N$ and any $j = 1, 2, \ldots, m$.

From Eq.(2.33) it follows that

$$
\begin{aligned}
\frac{\partial S_{11}}{\partial E\left(l_{j}\right)} = {} & \sum_{m=1}^{\infty}\left(\frac{1}{i\hbar}\right)^{2m}\sum_{k_{1}=2}^{N}\sum_{k_{2}=2}^{N}\cdots\sum_{k_{m}=2}^{N}\left|V_{1k_{1}}\right|^{2}\left|V_{1k_{2}}\right|^{2}\cdots\left|V_{1k_{m}}\right|^{2} \\
& \times\int_{-\infty}^{\infty}d\tau_{1}\int_{-\infty}^{\tau_{1}}d\tau_{2}\cdots\int_{-\infty}^{\tau_{2m-1}}d\tau_{2m} \\
& \times i\left[\delta\left(l_{j},k_{1}\right)\left(\tau_{1}-\tau_{2}\right)+\delta\left(l_{j},k_{2}\right)\left(\tau_{3}-\tau_{4}\right)+\cdots+\delta\left(l_{j},k_{m}\right)\left(\tau_{2m-1}-\tau_{2m}\right)\right] \\
& \times\exp\left[i\frac{B\left(k_{1}\right)}{2}\left(\tau_{1}^{2}-\tau_{2}^{2}\right)+\cdots+i\frac{B\left(k_{m}\right)}{2}\left(\tau_{2m-1}^{2}-\tau_{2m}^{2}\right)\right] \\
& \times\exp\left[iE\left(k_{1}\right)\left(\tau_{1}-\tau_{2}\right)+\cdots+iE\left(k_{m}\right)\left(\tau_{2m-1}-\tau_{2m}\right)\right],
\end{aligned} \tag{2.34}
$$

where $\delta\left(l_{j},k_{p}\right)$ is the Kronecker delta.

Next, I introduce the well-known change of variables

$$
\begin{aligned}
\tau_{1} &= x_{1}\in\left(-\infty,\infty\right), \\
\tau_{j+1} &= \tau_{j}-x_{j+1}, \quad\text{with}\quad x_{j+1}\in\left[0,\infty\right), \qquad j=1,2,\ldots,2m-1. \tag{2.35}
\end{aligned}
$$

From Eqs. (2.34) and (2.35) it follows that

$$
\begin{aligned}
\frac{\partial S_{11}}{\partial E\left(l_{j}\right)} = {} & \sum_{m=1}^{\infty}\left(\frac{1}{i\hbar}\right)^{m}\sum_{k_{1}=2}^{N}\sum_{k_{2}=2}^{N}\cdots\sum_{k_{m}=2}^{N}\left|V_{1k_{1}}\right|^{2}\left|V_{1k_{2}}\right|^{2}\cdots\left|V_{1k_{m}}\right|^{2} \\
& \times\int_{-\infty}^{\infty}dx_{1}\int_{0}^{\infty}dx_{2}\int_{0}^{\infty}dx_{3}\cdots\int_{0}^{\infty}dx_{2m} \\
& \times i\left[\delta\left(l_{j},k_{1}\right)x_{2}+\delta\left(l_{j},k_{2}\right)x_{4}+\cdots+\delta\left(l_{j},k_{m}\right)x_{2m}\right] \\
& \times F\left(x_{1},x_{2},\ldots,x_{2m}\right),
\end{aligned} \tag{2.36}
$$

where

$$
\begin{aligned}
F\left(x_{1}, x_{2}, \ldots, x_{2 m}\right) \;=\; & \exp\left[-\frac{i}{2} G\left(x_{2}, x_{4}, \ldots, x_{2 m-2}, x_{2 m}\right)\right] \\
& \times \exp\left[i\left\{B\left(k_{1}\right) x_{2}+B\left(k_{2}\right) x_{4}+\cdots+B\left(k_{m}\right) x_{2 m}\right\} x_{1}\right] \\
& \times \exp\left[-i\left\{B\left(k_{2}\right) x_{4}+B\left(k_{3}\right) x_{6}+\cdots+B\left(k_{m}\right) x_{2 m}\right\} x_{3}\right] \\
& \times \exp\left[-i\left\{B\left(k_{3}\right) x_{6}+B\left(k_{4}\right) x_{8}+\cdots+B\left(k_{m}\right) x_{2 m}\right\} x_{5}\right] \\
& \vdots \\
& \times \exp\left[-i\left\{B\left(k_{m}\right) x_{2 m}\right\} x_{2 m-1}\right],
\end{aligned}
\tag{2.37}
$$

and

$$
\begin{aligned}
G\left(x_{2}, x_{4}, \ldots, x_{2 m-2}, x_{2 m}\right) \;=\; & B\left(k_{1}\right)\left(x_{2}^{2}\right)+B\left(k_{2}\right)\left(2 x_{4} x_{2}+x_{4}^{2}\right) \\
& +B\left(k_{3}\right)\left(2 x_{6} x_{2}+2 x_{6} x_{4}+x_{6}^{2}\right) \\
& \vdots \\
& +B\left(k_{m}\right)\left(2 x_{2 m} x_{2}+\cdots+2 x_{2 m} x_{2 m-2}+x_{2 m}^{2}\right) \\
& -2\left[E\left(k_{1}\right) x_{2}+\cdots+E\left(k_{m}\right) x_{2 m}\right].
\end{aligned}
\tag{2.38}
$$

Upon integrating over x_1 in Eq.(2.36) one obtains

$$
\begin{aligned}
\frac{\partial S_{11}}{\partial E\left(l_j\right)} &= \sum_{m=1}^{\infty}\left(\frac{1}{i\hbar}\right)^m \sum_{k_1=2}^{N}\sum_{k_2=2}^{N}\cdots\sum_{k_m=2}^{N}\left|V_{1k_1}\right|^2\left|V_{1k_2}\right|^2\cdots\left|V_{1k_m}\right|^2 \\
&\times \int_0^{\infty}dx_2\int_0^{\infty}dx_3\cdots\int_0^{\infty}dx_{2m} \\
&\times i\left[\delta\left(l_j,k_1\right)x_2+\delta\left(l_j,k_2\right)x_4+\cdots+\delta\left(l_j,k_m\right)x_{2m}\right] \\
&\times \exp\left[-\frac{i}{2}G\left(x_2,x_4,\ldots,x_{2m-2},x_{2m}\right)\right] \\
&\times 2\pi\delta\left(B\left(k_1\right)x_2+B\left(k_2\right)x_4+\cdots+B\left(k_m\right)x_{2m}\right) \\
&\times \exp\left[-i\left\{B\left(k_2\right)x_4+B\left(k_3\right)x_6+\cdots+B\left(k_m\right)x_{2m}\right\}x_3\right] \\
&\times \exp\left[-i\left\{B\left(k_3\right)x_6+B\left(k_4\right)x_8+\cdots+B\left(k_m\right)x_{2m}\right\}x_5\right] \\
&\vdots \\
&\times \exp\left[-i\left\{B\left(k_m\right)x_{2m}\right\}x_{2m-1}\right].
\end{aligned}
\tag{2.39}
$$

If β_1 is an extremum, then all $B\left(k_j\right)>0$ (if $\beta_1=\max_k\beta_k$) or all $B\left(k_j\right)<0$ (if $\beta_1=\min_k\beta_k$). Therefore, $\delta\left(B\left(k_1\right)x_2+B\left(k_2\right)x_4+\cdots+B\left(k_m\right)x_{2m}\right)=0$ unless $x_2=x_4=\cdots=x_{2m}=0$. The presence of the term

$$
\left[\delta\left(l_j,k_1\right)x_2+\delta\left(l_j,k_2\right)x_4+\cdots+\delta\left(l_j,k_m\right)x_{2m}\right]
\tag{2.40}
$$

in the integrands of Eq.(2.39) ensures that each of the integrals is zero.

This argument can be made rigorous by regularizing the behavior of integrals at

$\pm\infty$, as follows

$$I_q \equiv \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dx_2 \int_0^{\infty} dx_3 \cdots \int_0^{\infty} dx_{2m} \, F(x_1, \ldots, x_{2m}) \, x_{2q}$$

$$= \lim_{\eta \to 0_+} \left\{ \int_0^{\infty} dx_2 \int_0^{\infty} dx_4 \cdots \int_0^{\infty} dx_{2m} \int_0^{\infty} dx_1 \int_0^{\infty} dx_3 \cdots \int_0^{\infty} dx_{2m-1} \right.$$

$$\times x_{2q} F(x_1, \ldots, x_{2m}) \exp\left[-\eta (x_1 + x_3 + \cdots + x_{2m-1}) \right]$$

$$+ \int_0^{\infty} dx_2 \int_0^{\infty} dx_4 \cdots \int_0^{\infty} dx_{2m} \int_{-\infty}^0 dx_1 \int_0^{\infty} dx_3 \cdots \int_0^{\infty} dx_{2m-1}$$

$$\left. \times x_{2q} F(x_1, \ldots, x_{2m}) \exp\left[-\eta (-x_1 + x_3 + \cdots + x_{2m-1}) \right] \right\}, \qquad (2.41)$$

for any $q = 1, 2, \ldots, m$. Upon integrating over the x_j with odd j in Eq.(2.41), one obtains

$$I_q = \lim_{\eta \to 0_+} \int_0^{\infty} dx_2 \int_0^{\infty} dx_4 \cdots \int_0^{\infty} dx_{2m} \, W(x_2, x_4, \ldots, x_{2m}; \eta), \qquad (2.42)$$

where

$$W(x_2, x_4, \ldots, x_{2m}; \eta) = \exp\left[-\frac{i}{2} G(x_2, x_4, \ldots, x_{2m}) \right]$$

$$\times \frac{2\eta x_{2q}}{[B(k_1) x_2 + B(k_2) x_4 + \cdots + B(k_m) x_{2m}]^2 + \eta^2}$$

$$\times \frac{1}{i [B(k_2) x_4 + B(k_3) x_6 + \cdots + B(k_m) x_{2m}] + \eta}$$

$$\vdots$$

$$\times \frac{1}{i [B(k_m) x_{2m}] + \eta}. \qquad (2.43)$$

Since either $B(k_j) > 0$ or $B(k_j) < 0$ for any k_j, from Eqs. (2.42) and (2.43) it

follows that

$$
\begin{aligned}
|I_q| \;\le\;& \lim_{\eta\to 0_+} \int_0^\infty dx_2 \int_0^\infty dx_4 \cdots \int_0^\infty dx_{2m} \; |W\left(x_2, x_4, \ldots, x_{2m}; \eta\right)| \\
=\;& \lim_{\eta\to 0_+} \int_0^{\eta/|B(k_1)|} dx_2 \int_0^{\eta/|B(k_2)|} dx_4 \cdots \int_0^{\eta/|B(k_m)|} dx_{2m} \\
& \times \frac{2\eta x_{2q}}{\left[B\left(k_1\right) x_2 + B\left(k_2\right) x_4 + \cdots + B\left(k_m\right) x_{2m}\right]^2 + \eta^2} \\
& \times \frac{1}{\sqrt{\left[B\left(k_2\right) x_4 + B\left(k_3\right) x_6 + \cdots + B\left(k_m\right) x_{2m}\right]^2 + \eta^2}} \\
& \;\;\vdots \\
& \times \frac{1}{\sqrt{\left[B\left(k_m\right) x_{2m}\right]^2 + \eta^2}},
\end{aligned}
\tag{2.44}
$$

and hence, Eq.(2.44) reduces to

$$
\begin{aligned}
|I_q| \;\le\;& \frac{1}{|B\left(k_1\right) B\left(k_2\right) \cdots B\left(k_m\right)|} \lim_{\eta\to 0_+} 2\eta \frac{\xi_q}{|B\left(k_q\right)|} \frac{1}{\left(\xi_1 + \xi_2 + \cdots + \xi_m\right)^2 + 1} \\
& \times \frac{1}{\sqrt{\left(\xi_2 + \xi_3 + \cdots + \xi_m\right)^2 + 1}} \cdots \frac{1}{\sqrt{\xi_m^2 + 1}} = 0,
\end{aligned}
\tag{2.45}
$$

where $\xi_j \in [0,1]$, for any $j = 1, 2, \ldots, m$. Eq.(2.45) shows that $I_q = 0$ for any $q = 1, 2, \ldots, m$, and consequently $\frac{\partial S_{11}}{\partial E(l_j)} = 0$ for any $E\left(l_j\right)$.

The fact that β_1 is maximal/minimal has played a key role in the arguments above. These arguments fail to hold if β_1 is not an extremum, since then the argument of $\delta\left(B\left(k_1\right) x_2 + B\left(k_2\right) x_4 + \cdots + B\left(k_m\right) x_{2m}\right)$ would have other zeros, besides the obvious $x_2 = x_4 = \cdots = x_{2m} = 0$.

In the last step, I reveal the connection between the BEF for a general N-level LZ-system and the exactly solvable bow-tie model [94], in which all levels interact with only one special level (SL). Indeed, since S_{11} does not depend on $E\left(l_j\right)$ if β_1 is maximal/minimal, I can safely set $E\left(l_j\right) = 0$ for any $l_j = 2, 3, \ldots, N$. The form for S_{11} (Eq.(2.33)) with all $E\left(l_j\right) = 0$ is exactly what one obtains for a bow-tie model if

the SL has slope β_1 (see Eq.(2.16)), and a perturbation expansion is being developed for it.

The integrals of the series expansion for S_{11} in the bow-tie model can be rather easily evaluated in any order. However, since the BEF holds for the bow-tie model, as shown by contour integration in [94], I only cite the statement from page 6947 of [94]: "This hypothesis is confirmed within the present model.", and refer to it for further details.

This concludes the proof of the Brundobler-Elser conjecture for a general N-level LZ-system.

CHAPTER III

NONEQUILIBRIUM DYNAMICS ACROSS A FESHBACH RESONANCE IN A
DEGENERATE FERMI GAS

In this Chapter I study the atom-molecule conversion in ultra-degenerate two-component Fermi gases subject to a linear downward sweep of a magnetic field across an s-wave Feshbach resonance (FR), in the spirit of experiments [16, 17, 18, 21]. Notwithstanding the differences in the details of these experiments, they all show a growth of the molecular conversion efficiency (MCE) with the inverse sweeping rate of the magnetic field, $\dot{B}^{-1}$, that saturates at values less than 100% in the adiabatic regime.

The attempts aimed at explaining the dependence of MCE on $\dot{B}$, resonance width, initial atomic density and temperature for two-component Fermi systems can be broadly classified into two classes: i) semi-phenomenological scenarios [51, 52] that reduce the many-body physics to a two-atom description modeled as a two-state Landau-Zener (LZ) system [46, 47] corresponding, respectively, to the free two-atom scattering state and the bound molecular state, and ii) numerical calculations in which many-body effects are only partially taken into account [53, 54, 55], and based on an effective Hamiltonian first proposed by Timmermans et $al.$ [99].

Class i) is appealing by its use of simple and intuitive physical pictures, but their predicted (temperature independent) upper MCE limit of 50% contradicts the experimentally observed far greater values [18, 21]. The recent experimental work by Hodby et $al.$ [21] also shows a pronounced T-dependence of this upper limit. The breakdown of the simple two-level LZ picture can be corrected only by introducing supplementary ad hoc assumptions in these semi-phenomenological scenarios, whereas

it emerges naturally from a bona fide many-body analysis (see below). The work in Class ii) has shown, albeit under some simplifying assumptions, the potential of the Hamiltonian [99] in analyzing the temperature dependence of the MCE saturation in the adiabatic regime. The disagreement between the results of these numerical calculations and experiment are mainly due to their use of a mean-field approximation for the bosonic degrees of freedom, in which only the zero-momentum bosonic-mode of the Hamiltonian [99] is retained.

Recently, Dobrescu and Pokrovsky [100] have developed a nonequilibrium theory, pertinent to both weak and strong atom-molecule coupling (measured in Fermi energy units), which allows for a full account of the effects of quantum statistics. The MCE is calculated in terms of real-time Green functions (GF), and represented as a power series in terms of a dimensionless parameter that depends only on the initial gas density and the LZ parameter. An exact evaluation of Feynman-Keldysh diagrams for second and fourth order processes reveals a clear deviation from the LZ transition probability at two-level crossing. This deviation, whose origins reside solely in many-body effects, signals a suppression of the LZ-predicted MCE even for moderately small values of $\dot{B}^{-1}$, as observed experimentally in [16, 17, 18, 21]. Equally important, the MCE result does not display an a priori upper limit of 50% at $T = 0$ as suggested in [51, 52]. This theory [100] is presented below.

The starting point of my analysis is the Hamiltonian [99, 101] describing a system of fermionic atoms FR-coupled to bosonic molecules, $\hat{H}(t) = \hat{H}_0(t) + \hat{V}$, with

$$\hat{H}_0(t) = \sum_{\psi=a,b,f} \sum_{\vec{p}} \varepsilon_\psi(\vec{p}, t)\hat{\psi}^\dagger(\vec{p})\hat{\psi}(\vec{p}), \tag{3.1}$$

$$\hat{V} = \frac{g}{\sqrt{\mathcal{V}}} \sum_{\vec{p},\vec{q}} \left[\hat{f}^\dagger\left(\vec{p}+\vec{q}\right)\hat{b}(\vec{q})\hat{a}(\vec{p}) + \text{h.c.} \right], \tag{3.2}$$

where $\hat{a}^\dagger(\vec{p})$, $\hat{a}(\vec{p})$ and $\hat{b}^\dagger(\vec{p})$, $\hat{b}(\vec{p})$ are fermionic creation and annihilation operators

describing atoms of momentum $\vec{p}$ and "spins" $\uparrow$ (a) and $\downarrow$ (b), respectively, and $\hat{f}^{\dagger}(\vec{p})$, $\hat{f}(\vec{p})$ play the same role for the bosonic molecules. Other quantities entering $\hat{H}$ are $\varepsilon_{\psi}(\vec{p}, t) = \widetilde{\varepsilon}_{\psi}(\vec{p}) - \mu_{\psi}B(t)$, with $\psi = a, b, f$, where μ_{ψ} is the projection of the magnetic moment along the direction of the magnetic field $B(t)$ with which interacts via Zeeman coupling, and $\widetilde{\varepsilon}_{\psi}(\vec{p})$ is the dispersion relation which accounts for the single-particle energy renormalization due to nonresonant collisions, and simply reduces to the kinetic energy $p^2/2m_{\psi}$ in a collisionless regime[1]; g is the two-atom-molecule coupling[2] which controls the FR width and $\mathcal{V}$ is the volume of system.

The free two-atom scattering state and the molecular state (MS) have different spin configurations and their coupling is mediated via the intra-atomic hyperfine interaction [102] which flips the electronic and nuclear spins of one of the colliding atoms. Depending on the magnetically tuned energy difference between the two states, the MS is quasi-bound (virtual) and belongs to a closed scattering channel if its energy exceeds that of the two-atom channel, becomes resonant with the latter when their energies are equal, and turns truly bound when its energy is the lesser of the two. This process is illustrated in Fig.2.

In order to probe the MCE dependence on $\dot{B}$, I evaluate real-time GF within the Keldysh-Schwinger formalism (KSF) [103]. The method is based on the use of a closed contour for time ordering, which runs from $-\infty$ to $+\infty$ and then back to $-\infty$. Both branches of the contour propagate along the real time axis and any point along them can be characterized by two parameters, written compactly as τ^{γ}, with τ being the time variable and γ a bookkeeping index that distinguishes between the forward

---

[1]The term collision refers here to scattering processes that cannot alter the number of atoms/molecules.

[2]$g \sim \epsilon_{hf}a^{3/2}$, where ϵ_{hf} is the strength of the hyperfine interaction responsible for the coupling between the electronic and nuclear spins, and a is the characteristic size of the molecule.
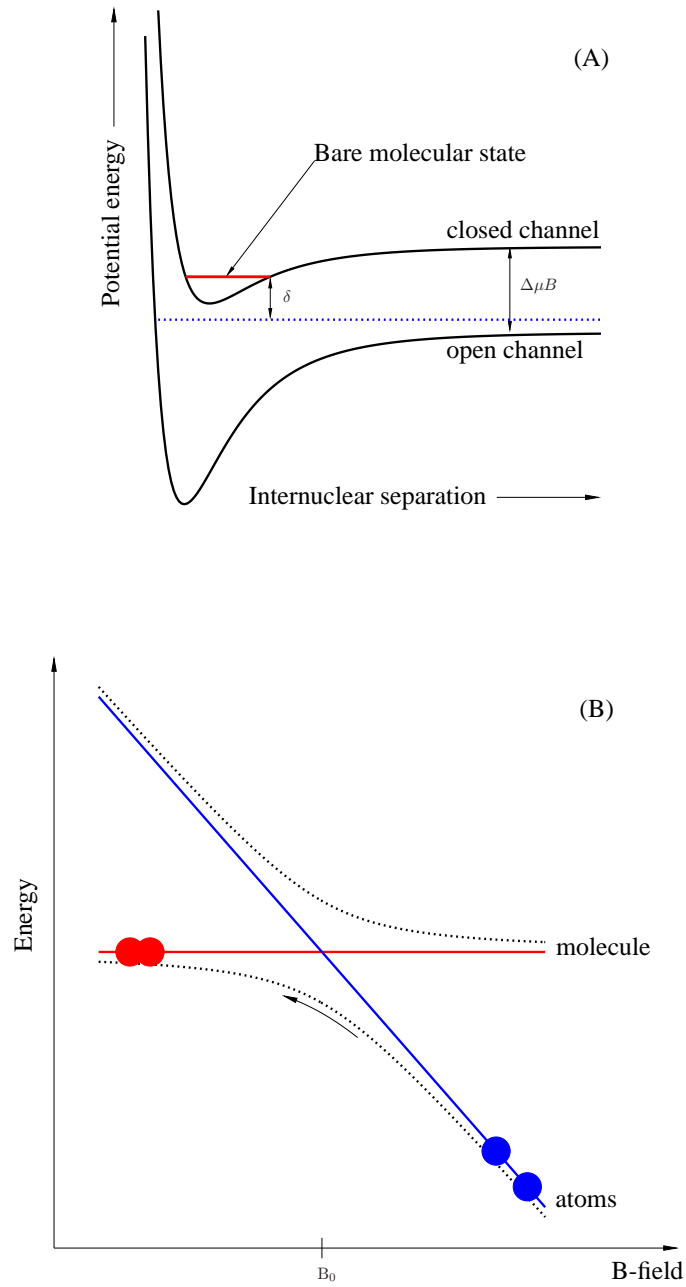
Fig. 2. A schematic two-atom scattering via a Feshbach resonance is shown. (A) A bound state in a closed channel can be brought in resonance with the scattering threshold of the open channel by adjusting the detuning δ. (B) A two-state Landau-Zener model corresponding, respectively, to the two-atom scattering state and the closed-channel molecular state.

($\gamma = +$) and reverse ($\gamma = -$) time directions. The basic quantities of KSF are the contour-ordered real-time GF:

$$i\mathcal{G}^{\alpha\beta}(\vec{p}_1, \tau_1; \vec{p}_2, \tau_2) = \left\langle \mathbf{T}_c \left[\hat{\psi}_H(\vec{p}_1, \tau_1^{\alpha}) \hat{\psi}_H^{\dagger}\left(\vec{p}_2, \tau_2^{\beta}\right) \right] \right\rangle, \tag{3.3}$$

with $\mathcal{G} \equiv \mathcal{A}, \mathcal{B}, \mathcal{F}$ for $\psi = a, b, f$, respectively, $\alpha, \beta = \pm$ and $\langle(\cdots)\rangle \equiv \text{Tr}[\hat{\rho}(t_0)(\cdots)]$. $\hat{\rho}(t_0)$ is the initial density operator at $t_0 = -\infty$, $\hat{\psi}_H$ are the Heisenberg-picture (HP) operators relative to t_0, and $\mathbf{T}_c$ is a contour-ordering operator. The corresponding free GF read

$$i\mathcal{G}_0^{\alpha\beta}(\vec{p}_1, \tau_1; \vec{p}_2, \tau_2) = \left\langle \mathbf{T}_c \left[\hat{\psi}_I(\vec{p}_1, \tau_1^{\alpha}) \hat{\psi}_I^{\dagger}\left(\vec{p}_2, \tau_2^{\beta}\right) \right] \right\rangle, \tag{3.4}$$

where $\hat{\psi}_I$ are the interaction-picture (IP) operators relative to t_0.

Upon expressing the $\hat{\psi}_H$ operators in terms of their IP form $\hat{\psi}_I$,

$$\hat{\psi}_H(t) = \hat{U}_I^{\dagger}(t, t_0)\hat{\psi}_I(t)\,\hat{U}_I(t, t_0), \tag{3.5}$$

and expanding the IP time-evolution operator, $\hat{U}_I(t, t_0)$, as a formal series in the coupling constant g, the following systematic expansion of the exact GF ensues:

$$
\begin{aligned}
i\mathcal{G}^{\alpha\beta}\left(\vec{k}_1, t_1; \vec{k}_2, t_2\right) &= i\mathcal{G}_0^{\alpha\beta}\left(\vec{k}_1, t_1; \vec{k}_2, t_2\right) \\
&+ \sum_{n=1}^{\infty} \left(\frac{1}{i\hbar}\right)^n \frac{1}{n!} \sum_{\{\gamma\}=\pm} (\gamma_1 \cdots \gamma_n) \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_n \\
&\times \left\langle \mathbf{T}_c \left[\hat{V}_I(\tau_1^{\gamma_1}) \cdots \hat{V}_I(\tau_n^{\gamma_n}) \hat{\psi}_I\left(\vec{k}_1, t_1^{\alpha}\right) \hat{\psi}_I^{\dagger}\left(\vec{k}_2, t_2^{\beta}\right) \right] \right\rangle,
\end{aligned}
\tag{3.6}
$$

where $\hat{V}_I$ is the IP form of $\hat{V}$, and the sum $\sum_{\{\gamma\}=\pm}$ runs over all n-tuples $(\gamma_1, \ldots, \gamma_n)$ with $\gamma_j = \pm$.

In the experiments [16, 17, 18, 21] an ultracold Fermi gas is prepared as an incoherent mixture of equal populations in each of two hyperfine states, and extreme quantum-degeneracy, at temperatures as low as $T \sim 0.05T_F$, has been reached [21],

where T_F is the Fermi temperature. In this regime the fall-off of the Fermi distribution from 1 to 0 takes place in an extremely narrow energy interval $\sim 0.05\varepsilon_F$, where ε_F is the Fermi energy, and the fuzziness of the Fermi surface becomes virtually unimportant. In this vein, I take $\hat{\rho}(t_0) = |\Phi_0\rangle \langle\Phi_0|$, with

$$|\Phi_0\rangle = \prod_{\vec{p}}^{<} \hat{a}^\dagger(\vec{p})\hat{b}^\dagger(\vec{p})|\text{VAC}\rangle, \tag{3.7}$$

where $|\text{VAC}\rangle$ is the vacuum state, and $\prod^{<}$ represents a product over momenta $\vec{p}$, subject to restriction $0 \leq \widetilde{\varepsilon}(\vec{p}) \leq \varepsilon_F$. Since the two equally populated components of the Fermi gas correspond to two different internal states of the same atom species, I consider the same dispersion for them, i.e. $\widetilde{\varepsilon}_a(\vec{p}) = \widetilde{\varepsilon}_b(\vec{p}) \equiv \widetilde{\varepsilon}(\vec{p})$.

Due to the form of $|\Phi_0\rangle$, the free GF $\mathcal{G}_0^{\alpha\beta}(\vec{p}_1, \tau_1; \vec{p}_2, \tau_2) \propto \delta(\vec{p}_1, \vec{p}_2)$, where $\delta(\vec{p}_1, \vec{p}_2)$ is the Kronecker delta, and their expressions are

$$i\mathcal{G}_0^{+-}(\vec{p}; \tau_1, \tau_2) = -\theta(\varepsilon_F - \widetilde{\varepsilon}_\psi(\vec{p})) \exp\left[\frac{i}{\hbar}\int_{\tau_1}^{\tau_2} \varepsilon_\psi(\vec{p}, \tau)d\tau\right], \tag{3.8}$$

$$i\mathcal{G}_0^{-+}(\vec{p}; \tau_1, \tau_2) = \theta(\widetilde{\varepsilon}_\psi(\vec{p}) - \varepsilon_F) \exp\left[\frac{i}{\hbar}\int_{\tau_1}^{\tau_2} \varepsilon_\psi(\vec{p}, \tau)d\tau\right], \tag{3.9}$$

with $\mathcal{G} \equiv \mathcal{A}, \mathcal{B}$ for $\psi = a, b$, respectively, and

$$i\mathcal{F}_0^{+-}(\vec{p}; \tau_1, \tau_2) = 0, \tag{3.10}$$

$$i\mathcal{F}_0^{-+}(\vec{p}; \tau_1, \tau_2) = \exp\left[\frac{i}{\hbar}\int_{\tau_1}^{\tau_2} \varepsilon_f(\vec{p}, \tau)d\tau\right], \tag{3.11}$$

and finally

$$\mathcal{G}^{++}(\vec{p}; \tau_1, \tau_2) = \theta(x)\mathcal{G}^{-+}(\vec{p}; \tau_1, \tau_2) + \theta(-x)\mathcal{G}^{+-}(\vec{p}; \tau_1, \tau_2), \tag{3.12}$$

$$\mathcal{G}^{--}(\vec{p}; \tau_1, \tau_2) = \theta(x)\mathcal{G}^{+-}(\vec{p}; \tau_1, \tau_2) + \theta(-x)\mathcal{G}^{-+}(\vec{p}; \tau_1, \tau_2), \tag{3.13}$$

for any $\mathcal{G} \equiv \mathcal{A}, \mathcal{B}, \mathcal{F}$, where $x = \tau_1 - \tau_2$ and $\theta(x)$ is the Heaviside function.

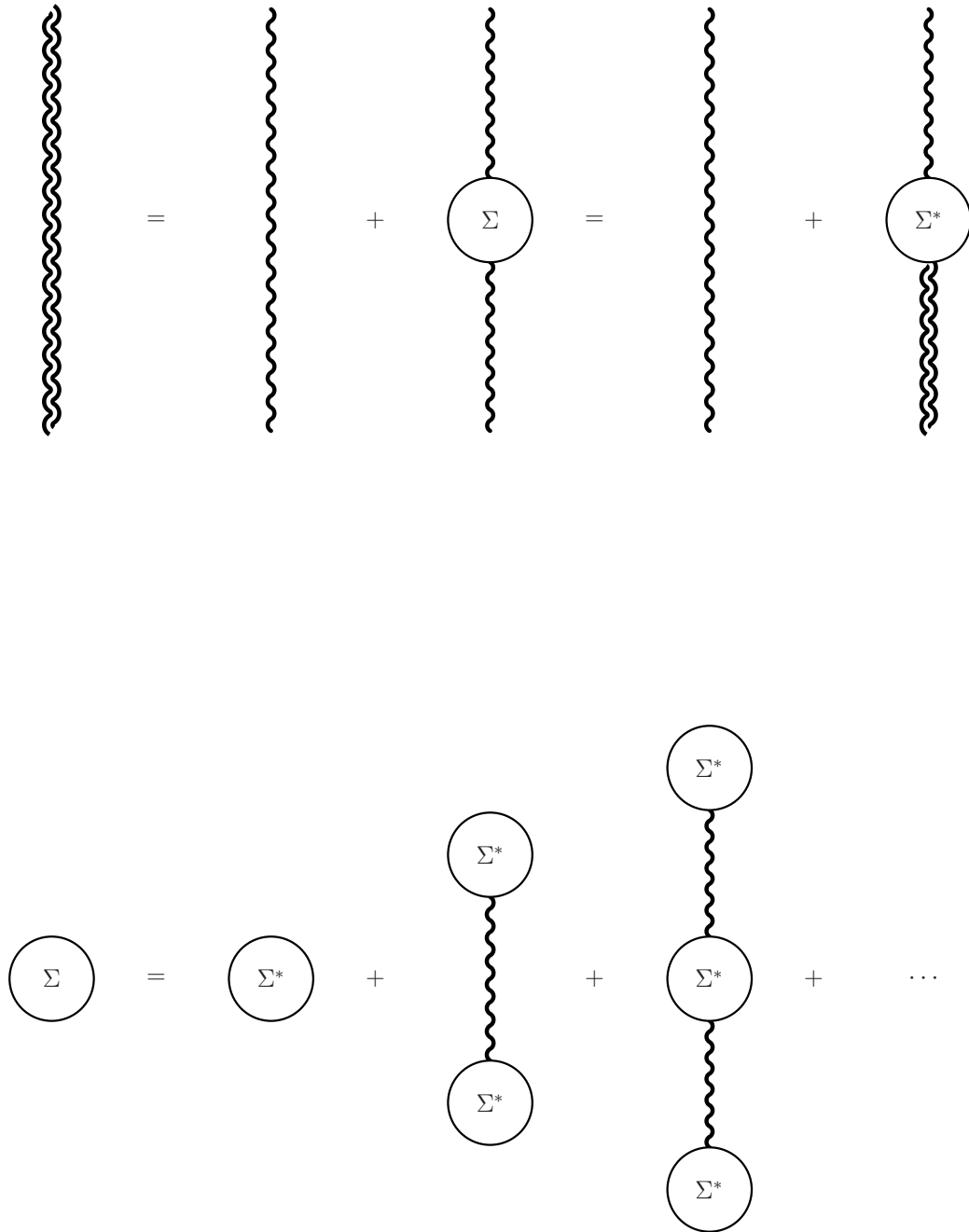Fig. 3. Schematic representation of Dyson's equation. The double and simple wiggly lines represent, respectively, the exact and free GF. $\sum$ and $\sum^*$ are the self-energy and proper self-energy, respectively.

Each average corresponding to the terms in Eq.(3.6) can be performed by means of a generalized version of Wick's theorem in which the contractions are defined with respect to the contour-ordering operator $\mathbf{T}_c$, and a Feynman diagram is associated with each way of contracting the field operators into pairs [103]. These diagrams have the same topology as those occurring in the ordinary quantum field theory (OQFT) for systems in equilibrium [104, 105], the only difference being an additional label $\gamma = \pm$ that has to be attached to each interaction vertex. As in OQFT, the disconnected diagrams corresponding to vacuum polarization vanish [103], and only topologically distinct diagrams need to be considered. The exact GF consists of the free GF plus all connected terms with a free GF at each end, i.e.

$$
\begin{aligned}
\mathcal{G}^{\alpha\beta}\left(\vec{k}_1, t_1; \vec{k}_2, t_2\right) &= \mathcal{G}_0^{\alpha\beta}\left(\vec{k}_1, t_1; \vec{k}_2, t_2\right) + \sum_{\vec{p}_1, \vec{p}_2} \sum_{\gamma_1, \gamma_2 = \pm} \gamma_1 \gamma_2 \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2 \\
&\times \mathcal{G}_0^{\alpha\gamma_1}\left(\vec{k}_1, t_1; \vec{p}_1, \tau_1\right) \left(\sum\right)^{\gamma_1\gamma_2} (\vec{p}_1, \tau_1; \vec{p}_2, \tau_2) \\
&\times \mathcal{G}_0^{\gamma_2\beta}\left(\vec{p}_2, \tau_2; \vec{k}_2, t_2\right),
\end{aligned}
$$

where $\left(\sum\right)^{\gamma_1\gamma_2}(\vec{p}_1, \tau_1; \vec{p}_2, \tau_2)$ is the self-energy, and

$$
\begin{aligned}
\left(\sum\right)^{\gamma_1\gamma_2}(\vec{p}_1, \tau_1; \vec{p}_2, \tau_2) &= \left(\sum{}^{*}\right)^{\gamma_1\gamma_2}(\vec{p}_1, \tau_1; \vec{p}_2, \tau_2) \\
&+ \sum_{\vec{q}_1, \vec{q}_2} \sum_{\lambda_1, \lambda_2 = \pm} \lambda_1 \lambda_2 \int_{-\infty}^{+\infty} d\sigma_1 \int_{-\infty}^{+\infty} d\sigma_2 \\
&\times \left(\sum{}^{*}\right)^{\gamma_1\lambda_1}(\vec{p}_1, \tau_1; \vec{q}_1, \sigma_1) \, \mathcal{G}_0^{\lambda_1\lambda_2}(\vec{q}_1, \sigma_1; \vec{q}_2, \sigma_2) \\
&\times \left(\sum{}^{*}\right)^{\lambda_2\gamma_2}(\vec{q}_2, \sigma_2; \vec{p}_2, \tau_2) + \cdots
\end{aligned}
$$

The proper self-energy $\left(\sum{}^{*}\right)^{\gamma_1\gamma_2}(\vec{p}_1, \tau_1; \vec{p}_2, \tau_2)$ is the sum of all proper self-energy insertions, $\sum{}^{*} = \sum{}^{*}_{(1)} + \sum{}^{*}_{(2)} + \cdots$, where each $\sum{}^{*}_{(j)}$ cannot be further separated into two connected pieces by cutting a single free GF line. All these relations are summarized in Fig.3. Finally, Dyson's equation which connects the exact and free
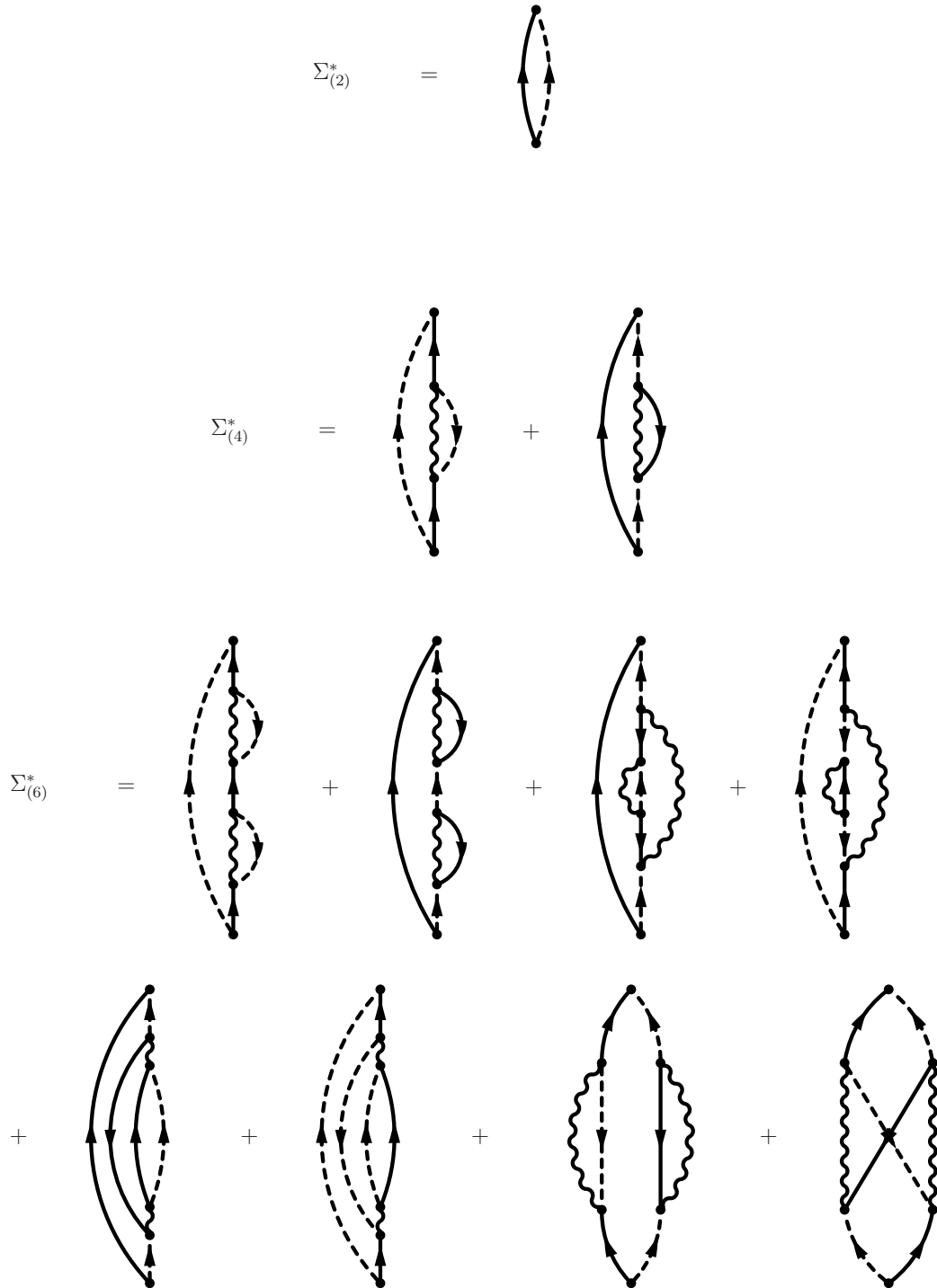
Fig. 4. Bosonic proper self-energy insertions up to the 6-th order.
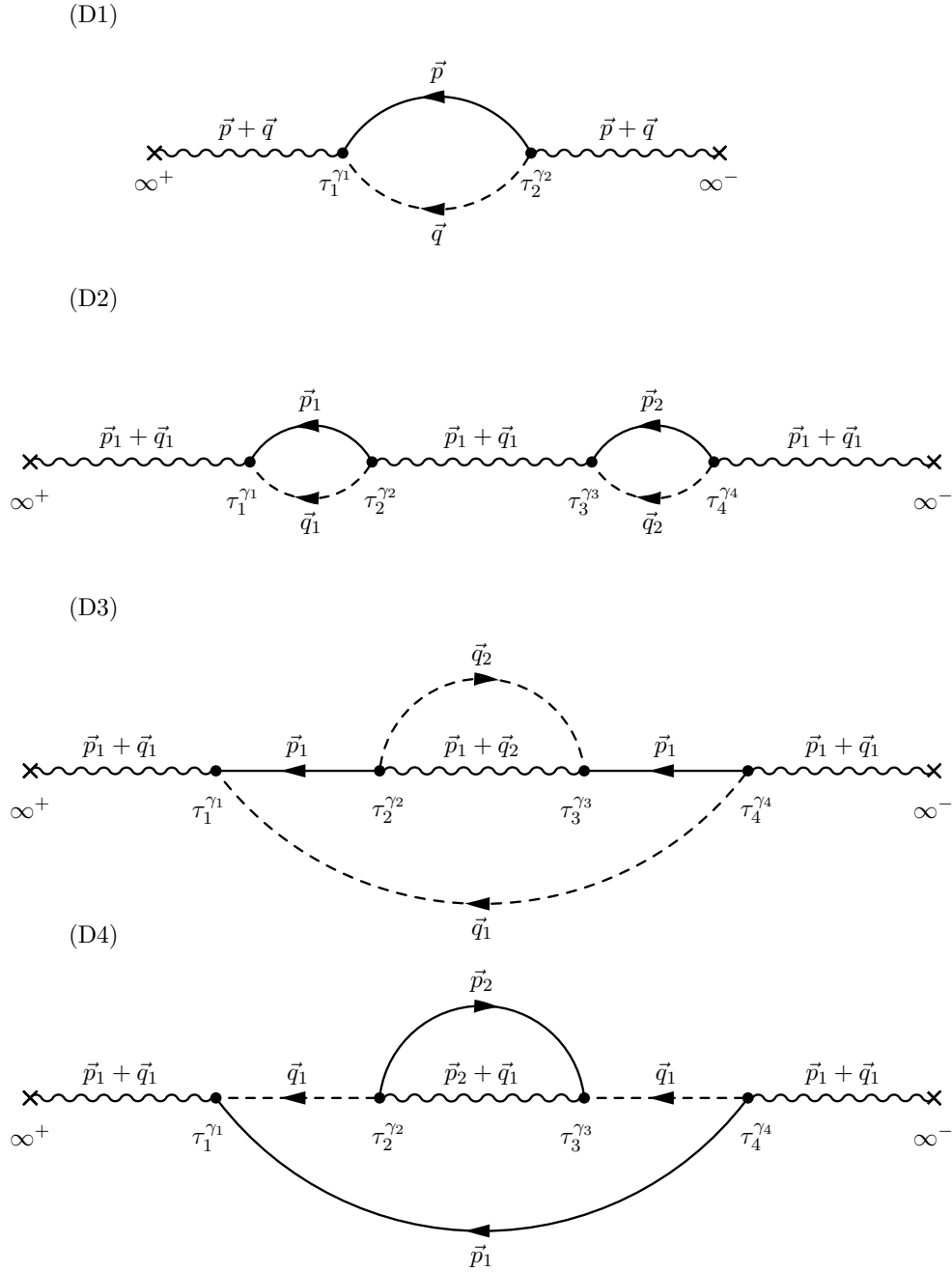
(D1)

(D2)

(D3)

(D4)

Fig. 5. Feynman-Keldysh diagrams for second (D1) and fourth order (D2 - D4) processes. The free Green functions are represented by continuous lines for a-fermions ($\mathcal{A}_0^{\gamma_i \gamma_j}$), by dashed lines for b-fermions ($\mathcal{B}_0^{\gamma_i \gamma_j}$), and by wiggly lines for bosons ($\mathcal{F}_0^{\gamma_i \gamma_j}$).

GF via the proper self-energy reads

$$\mathcal{G}^{\alpha\beta}\left(\vec{k}_1, t_1; \vec{k}_2, t_2\right) = \mathcal{G}_0^{\alpha\beta}\left(\vec{k}_1, t_1; \vec{k}_2, t_2\right) + \sum_{\vec{p}_1, \vec{p}_2} \sum_{\gamma_1, \gamma_2 = \pm} \gamma_1 \gamma_2 \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2$$

$$\times \mathcal{G}_0^{\alpha\gamma_1}\left(\vec{k}_1, t_1; \vec{p}_1, \tau_1\right) \left(\sum{}^*\right)^{\gamma_1 \gamma_2}\left(\vec{p}_1, \tau_1; \vec{p}_2, \tau_2\right)$$

$$\times \mathcal{G}^{\gamma_2 \beta}\left(\vec{p}_2, \tau_2; \vec{k}_2, t_2\right).$$

Since $\hat{f}_I\left(\vec{p}, t\right)|\Phi_0\rangle = 0$ for any $\vec{p}$ and t, and $\hat{V}_I \sim \hat{f}_I + \hat{f}_I^\dagger$, it follows that all the proper self-energy insertions can have only an even number of vertices, i.e. $\sum^* = \sum_{(2)}^* + \sum_{(4)}^* + \sum_{(6)}^* + \cdots$. The contributions to the bosonic $\sum^*$, up to the 6-th order, are shown in Fig.4.

The average number of molecules at time t is given by

$$\left\langle \hat{N}_f \right\rangle (t) = i \sum_{\vec{k}} \mathcal{F}^{+-}\left(\vec{k}, t; \vec{k}, t\right). \tag{3.14}$$

In the experiments [16, 17, 18, 21] the magnetic field is being linearly swept from well above its FR value, B_0, where the molecular channel is closed, to far below B_0 into a region where bound molecules exist. Since the main interest lies in analyzing the dependence of MCE on $\dot{B}^{-1}$, and not the behavior of the average number of molecules in time, I set the initial time of atomic gas preparation at $t_0 = -\infty$, and the molecule-counting time at $t_m = \infty$. The Feynman diagrams representing the contribution from second and fourth order processes to $\left\langle \hat{N}_f \right\rangle (\infty)$ are shown in Fig.5.

The (D1) diagrams contribute as

$$\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^2 \sum_{\vec{p},\vec{q}} \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2$$

$$\times i\mathcal{F}_0^{-+}(\vec{p}+\vec{q};\infty,\tau_1)\, i\mathcal{F}_0^{-+}(\vec{p}+\vec{q};\tau_2,\infty)\, i\mathcal{A}_0^{+-}(\vec{p};\tau_1,\tau_2)\, i\mathcal{B}_0^{+-}(\vec{q};\tau_1,\tau_2)$$

$$= \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^2 \sum_{\vec{p},\vec{q}}^{<} \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2$$

$$\times \exp\left[-i\frac{\dot{\Omega}}{2}\left(\tau_1 + \frac{\varpi(\vec{p},\vec{q})}{\dot{\Omega}}\right)^2\right] \exp\left[i\frac{\dot{\Omega}}{2}\left(\tau_2 + \frac{\varpi(\vec{p},\vec{q})}{\dot{\Omega}}\right)^2\right]$$

$$= \frac{N_0}{2} \times \left(2\pi\frac{g^2}{\hbar^2\dot{\Omega}}\frac{n_0}{2}\right), \tag{3.15}$$

where $\hbar\dot{\Omega} \equiv (\mu_f - \mu_a - \mu_b)\dot{B} > 0$, N_0 is the total number of atoms present in the system before the magnetic field is applied, and $n_0 = N_0/\mathcal{V}$ is the initial density. The rest of notations are as follows

$$\hbar\omega(\vec{p},\vec{q};\tau) \equiv \varepsilon_a(\vec{p},\tau) + \varepsilon_b(\vec{q},\tau) - \varepsilon_f(\vec{p}+\vec{q},\tau) \equiv \hbar\varpi(\vec{p},\vec{q}) + \hbar\dot{\Omega}\tau,$$

$$\sum_{\vec{p}}^{<} \equiv \sum_{\substack{\vec{p} \\ \tilde{\varepsilon}(\vec{p})\leq\varepsilon_F}}, \qquad \sum_{\vec{p}}^{>} \equiv \sum_{\substack{\vec{p} \\ \tilde{\varepsilon}(\vec{p})>\varepsilon_F}}.$$

The contribution from the (D2) diagrams is

$$A \equiv \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\gamma_2,\gamma_3=\pm}(-\gamma_2\gamma_3)\sum_{\vec{p}_1,\vec{q}_1}\sum_{\vec{p}_2,\vec{q}_2}\delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right)$$

$$\times \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4$$

$$\times i\mathcal{F}_0^{++}(\vec{p}_1+\vec{q}_1;\infty,\tau_1)\, i\mathcal{F}_0^{\gamma_2\gamma_3}(\vec{p}_1+\vec{q}_1;\tau_2,\tau_3)\, i\mathcal{F}_0^{--}(\vec{p}_1+\vec{q}_1;\tau_4,\infty)$$

$$\times i\mathcal{A}_0^{+\gamma_2}(\vec{p}_1;\tau_1,\tau_2)\, i\mathcal{B}_0^{+\gamma_2}(\vec{q}_1;\tau_1,\tau_2)$$

$$\times i\mathcal{A}_0^{\gamma_3-}(\vec{p}_2;\tau_3,\tau_4)\, i\mathcal{B}_0^{\gamma_3-}(\vec{q}_2;\tau_3,\tau_4) = \sum_{j=1}^{5} A_j.$$

The term A_1 is given by

$$
\begin{aligned}
A_1 &\equiv (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1}\sum_{\vec{p}_2,\vec{q}_2} \delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right) \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \\
&\quad \times \theta\left(\tau_1-\tau_2\right)\theta\left(\tau_2-\tau_3\right) i\mathcal{F}_0^{-+}\left(\vec{p}_1+\vec{q}_1;\tau_4,\tau_1\right) i\mathcal{F}_0^{-+}\left(\vec{p}_1+\vec{q}_1;\tau_2,\tau_3\right) \\
&\quad \times i\mathcal{A}_0^{-+}\left(\vec{p}_1;\tau_1,\tau_2\right) i\mathcal{B}_0^{-+}\left(\vec{q}_1;\tau_1,\tau_2\right) i\mathcal{A}_0^{+-}\left(\vec{p}_2;\tau_3,\tau_4\right) i\mathcal{B}_0^{+-}\left(\vec{q}_2;\tau_3,\tau_4\right)
\end{aligned}
$$

$$
\begin{aligned}
&= (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1}^{>}\sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right) \\
&\quad \times \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4\ \theta\left(\tau_1-\tau_2\right)\theta\left(\tau_2-\tau_3\right) \\
&\quad \times \exp\left[i\frac{\dot{\Omega}}{2}\left(\tau_2+\frac{\varpi(\vec{p}_1,\vec{q}_1)}{\dot{\Omega}}\right)^2\right]\exp\left[-i\frac{\dot{\Omega}}{2}\left(\tau_1+\frac{\varpi(\vec{p}_1,\vec{q}_1)}{\dot{\Omega}}\right)^2\right] \\
&\quad \times \exp\left[i\frac{\dot{\Omega}}{2}\left(\tau_4+\frac{\varpi(\vec{p}_2,\vec{q}_2)}{\dot{\Omega}}\right)^2\right]\exp\left[-i\frac{\dot{\Omega}}{2}\left(\tau_3+\frac{\varpi(\vec{p}_2,\vec{q}_2)}{\dot{\Omega}}\right)^2\right]
\end{aligned}
$$

$$
\begin{aligned}
&= (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sqrt{\frac{2\pi}{-i\dot{\Omega}}} \sum_{\vec{p}_1,\vec{q}_1}^{>}\sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right) \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_3 \\
&\quad \times \exp\left[-i\frac{\dot{\Omega}}{2}\left[\left(\tau_1+\frac{\varpi(\vec{p}_1,\vec{q}_1)}{\dot{\Omega}}\right)^2 - \left(\tau_2+\frac{\varpi(\vec{p}_1,\vec{q}_1)}{\dot{\Omega}}\right)^2 + \left(\tau_3+\frac{\varpi(\vec{p}_2,\vec{q}_2)}{\dot{\Omega}}\right)^2\right]\right]
\end{aligned}
$$

$$
\begin{aligned}
&= (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sqrt{\frac{2\pi}{-i\dot{\Omega}}} \sum_{\vec{p}_1,\vec{q}_1}^{>}\sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right) \int_{-\infty}^{+\infty} dx \int_{0}^{\infty} dy \int_{0}^{\infty} dz \\
&\quad \times \exp\left[-i\frac{\dot{\Omega}}{2}\left(x-z+\frac{\varpi(\vec{p}_2,\vec{q}_2)}{\dot{\Omega}}\right)^2\right]\exp\left[-i\dot{\Omega}y\left(z+\frac{\varpi(\vec{p}_1,\vec{q}_1)-\varpi(\vec{p}_2,\vec{q}_2)}{\dot{\Omega}}\right)\right]
\end{aligned}
$$

$$
\begin{aligned}
&= (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \left(\frac{2\pi}{\dot{\Omega}}\right) \sum_{\vec{p}_1,\vec{q}_1}^{>}\sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right) \int_{0}^{\infty} dy \int_{0}^{\infty} dz \\
&\quad \times \exp\left[-i\dot{\Omega}y\left(z+\frac{\varpi(\vec{p}_1,\vec{q}_1)-\varpi(\vec{p}_2,\vec{q}_2)}{\dot{\Omega}}\right)\right],
\end{aligned}
$$

where the change of variables used is

$$
\begin{aligned}
\tau_1 &= x \in (-\infty, \infty), \\
\tau_2 &= x - y, \quad y \in [0, \infty), \\
\tau_3 &= x - y - z, \quad z \in [0, \infty).
\end{aligned}
$$

The term A_2 is given by

$$
\begin{aligned}
A_2 &\equiv (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1}\sum_{\vec{p}_2,\vec{q}_2} \delta\left(\vec{p}_1 + \vec{q}_1, \vec{p}_2 + \vec{q}_2\right) \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \\
&\quad \times \theta\left(\tau_4 - \tau_3\right)\theta\left(\tau_3 - \tau_2\right) i\mathcal{F}_0^{-+}\left(\vec{p}_1 + \vec{q}_1; \tau_4, \tau_1\right) i\mathcal{F}_0^{-+}\left(\vec{p}_1 + \vec{q}_1; \tau_2, \tau_3\right) \\
&\quad \times i\mathcal{A}_0^{+-}\left(\vec{p}_1; \tau_1, \tau_2\right) i\mathcal{B}_0^{+-}\left(\vec{q}_1; \tau_1, \tau_2\right) i\mathcal{A}_0^{-+}\left(\vec{p}_2; \tau_3, \tau_4\right) i\mathcal{B}_0^{-+}\left(\vec{q}_2; \tau_3, \tau_4\right)
\end{aligned}
$$

$$
\begin{aligned}
&= (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1}\sum_{\vec{p}_2,\vec{q}_2} \delta\left(\vec{p}_1 + \vec{q}_1, \vec{p}_2 + \vec{q}_2\right) \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \\
&\quad \times \theta\left(\tau_1 - \tau_2\right)\theta\left(\tau_2 - \tau_3\right)\left(i\mathcal{F}_0^{-+}\left(\vec{p}_1 + \vec{q}_1; \tau_4, \tau_1\right)\right)^*\left(i\mathcal{F}_0^{-+}\left(\vec{p}_1 + \vec{q}_1; \tau_2, \tau_3\right)\right)^* \\
&\quad \times \left(i\mathcal{A}_0^{-+}\left(\vec{p}_1; \tau_1, \tau_2\right)\right)^*\left(i\mathcal{B}_0^{-+}\left(\vec{q}_1; \tau_1, \tau_2\right)\right)^*\left(i\mathcal{A}_0^{+-}\left(\vec{p}_2; \tau_3, \tau_4\right)\right)^*\left(i\mathcal{B}_0^{+-}\left(\vec{q}_2; \tau_3, \tau_4\right)\right)^*.
\end{aligned}
$$

The sum $A_1 + A_2$ becomes

$$
\begin{aligned}
A_1 + A_2 &= (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \left(\frac{2\pi}{\dot{\Omega}}\right) \sum_{\vec{p}_1,\vec{q}_1}^{>}\sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1 + \vec{q}_1, \vec{p}_2 + \vec{q}_2\right) \\
&\quad \times \int_{-\infty}^{\infty} dy \int_0^{\infty} dz \exp\left[-i\dot{\Omega}y\left(z + \frac{\varpi(\vec{p}_1, \vec{q}_1) - \varpi(\vec{p}_2, \vec{q}_2)}{\dot{\Omega}}\right)\right] \\
&= (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \left(\frac{2\pi}{\dot{\Omega}}\right) \sum_{\vec{p}_1,\vec{q}_1}^{>}\sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1 + \vec{q}_1, \vec{p}_2 + \vec{q}_2\right) \\
&\quad \times \frac{2\pi}{\dot{\Omega}} \int_0^{\infty} \delta\left(z + \frac{\varpi(\vec{p}_1, \vec{q}_1) - \varpi(\vec{p}_2, \vec{q}_2)}{\dot{\Omega}}\right) dz = 0,
\end{aligned}
$$

since $\dot{\Omega} > 0$ and $\delta\left(\vec{p}_1 + \vec{q}_1, \vec{p}_2 + \vec{q}_2\right)\frac{\varpi(\vec{p}_1, \vec{q}_1) - \varpi(\vec{p}_2, \vec{q}_2)}{\dot{\Omega}} > 0$ in the sum above.

The term A_3 is given by

$$
\begin{aligned}
A_3 \equiv & (-) \left(\frac{g}{\hbar\sqrt{\mathcal{V}}} \right)^4 \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1 + \vec{q}_1, \vec{p}_2 + \vec{q}_2\right) \\
& \times \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \; \theta\left(\tau_2 - \tau_3\right) \theta\left(\tau_2 - \tau_1\right) \\
& \times \exp\left[\frac{i}{\hbar} \int_{\tau_1}^{\tau_2} \left[\varepsilon_a(\vec{p}_1, \tau) + \varepsilon_b(\vec{q}_1, \tau) - \varepsilon_f(\vec{p}_1 + \vec{q}_1, \tau) \right] d\tau \right] \\
& \times \exp\left[\frac{i}{\hbar} \int_{\tau_3}^{\tau_4} \left[\varepsilon_a(\vec{p}_2, \tau) + \varepsilon_b(\vec{q}_2, \tau) - \varepsilon_f(\vec{p}_2 + \vec{q}_2, \tau) \right] d\tau \right]
\end{aligned}
$$

$$
\begin{aligned}
= & (-) \left(\frac{g}{\hbar\sqrt{\mathcal{V}}} \right)^4 \sqrt{\frac{2\pi}{-i\dot{\Omega}}} \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1 + \vec{q}_1, \vec{p}_2 + \vec{q}_2\right) \int_{-\infty}^{+\infty} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \int_{-\infty}^{\tau_2} d\tau_3 \\
& \times \exp\left[-i\frac{\dot{\Omega}}{2} \left[\left(\tau_1 + \frac{\varpi(\vec{p}_1, \vec{q}_1)}{\dot{\Omega}} \right)^2 - \left(\tau_2 + \frac{\varpi(\vec{p}_1, \vec{q}_1)}{\dot{\Omega}} \right)^2 + \left(\tau_3 + \frac{\varpi(\vec{p}_2, \vec{q}_2)}{\dot{\Omega}} \right)^2 \right] \right]
\end{aligned}
$$

$$
\begin{aligned}
= & (-) \left(\frac{g}{\hbar\sqrt{\mathcal{V}}} \right)^4 \sqrt{\frac{2\pi}{-i\dot{\Omega}}} \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1 + \vec{q}_1, \vec{p}_2 + \vec{q}_2\right) \int_{-\infty}^{+\infty} dx \int_0^{\infty} dy \int_0^{\infty} dz \\
& \times \exp\left[-i\frac{\dot{\Omega}}{2} \left(x - y - z + \frac{\varpi(\vec{p}_2, \vec{q}_2)}{\dot{\Omega}} \right)^2 \right] \exp\left[i\dot{\Omega} \left(z + \frac{\varpi(\vec{p}_1, \vec{q}_1) - \varpi(\vec{p}_2, \vec{q}_2)}{\dot{\Omega}} \right) y \right]
\end{aligned}
$$

$$
\begin{aligned}
= & (-) \left(\frac{g}{\hbar\sqrt{\mathcal{V}}} \right)^4 \left(\frac{2\pi}{\dot{\Omega}} \right) \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1 + \vec{q}_1, \vec{p}_2 + \vec{q}_2\right) \\
& \times \int_0^{\infty} dy \int_0^{\infty} dz \exp\left[i\dot{\Omega} \left(z + \frac{\varpi(\vec{p}_1, \vec{q}_1) - \varpi(\vec{p}_2, \vec{q}_2)}{\dot{\Omega}} \right) y \right],
\end{aligned}
$$

where the change of variables used is

$$
\begin{aligned}
\tau_2 &= x \in (-\infty, \infty), \\
\tau_1 &= x - y, \quad y \in [0, \infty), \\
\tau_3 &= x - z, \quad z \in [0, \infty).
\end{aligned}
$$

The term A_4 is given by

$$
\begin{aligned}
A_4 &\equiv (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1}\sum_{\vec{p}_2,\vec{q}_2} \delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right) \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \\
&\quad \times \theta\left(\tau_2-\tau_3\right)\theta\left(\tau_2-\tau_1\right)\left(i\mathcal{F}_0^{-+}\left(\vec{p}_1+\vec{q}_1;\tau_4,\tau_1\right)\right)^*\left(i\mathcal{F}_0^{-+}\left(\vec{p}_1+\vec{q}_1;\tau_2,\tau_3\right)\right)^* \\
&\quad \times \left(i\mathcal{A}_0^{+-}\left(\vec{p}_1;\tau_1,\tau_2\right)\right)^*\left(i\mathcal{B}_0^{+-}\left(\vec{q}_1;\tau_1,\tau_2\right)\right)^* \\
&\quad \times \left(i\mathcal{A}_0^{+-}\left(\vec{p}_2;\tau_3,\tau_4\right)\right)^*\left(i\mathcal{B}_0^{+-}\left(\vec{q}_2;\tau_3,\tau_4\right)\right)^*.
\end{aligned}
$$

The sum $A_3 + A_4$ becomes

$$
\begin{aligned}
A_3 + A_4 &= (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4\left(\frac{2\pi}{\dot{\Omega}}\right)\sum_{\vec{p}_1,\vec{q}_1}^{<}\sum_{\vec{p}_2,\vec{q}_2}^{<}\delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right) \\
&\quad \times \int_{-\infty}^{\infty} dy \int_0^{\infty} dz \exp\left[-i\dot{\Omega}\left(z+\frac{\varpi(\vec{p}_1,\vec{q}_1)-\varpi(\vec{p}_2,\vec{q}_2)}{\dot{\Omega}}\right)y\right] \\
&= (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4\left(\frac{2\pi}{\dot{\Omega}}\right)^2\sum_{\vec{p}_1,\vec{q}_1}^{<}\sum_{\vec{p}_2,\vec{q}_2}^{<}\delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right) \\
&\quad \times \int_0^{\infty}\delta\left(z+\frac{\varpi(\vec{p}_1,\vec{q}_1)-\varpi(\vec{p}_2,\vec{q}_2)}{\dot{\Omega}}\right)dz \\
&= (-)\frac{1}{2}\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4\left(\frac{2\pi}{\dot{\Omega}}\right)^2\sum_{\vec{p}_1,\vec{q}_1}^{<}\sum_{\vec{p}_2,\vec{q}_2}^{<}\delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right).
\end{aligned}
$$

The term A_5 is given by

$$
\begin{aligned}
A_5 &\equiv \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4\sum_{\vec{p}_1,\vec{q}_1}^{<}\sum_{\vec{p}_2,\vec{q}_2}^{<}\delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right)\int_{-\infty}^{+\infty}d\tau_1\cdots\int_{-\infty}^{+\infty}d\tau_4 \\
&\quad \times \exp\left[-i\frac{\dot{\Omega}}{2}\left(\tau_1+\frac{\varpi(\vec{p}_1,\vec{q}_1)}{\dot{\Omega}}\right)^2\right]\exp\left[i\frac{\dot{\Omega}}{2}\left(\tau_2+\frac{\varpi(\vec{p}_1,\vec{q}_1)}{\dot{\Omega}}\right)^2\right] \\
&\quad \times \exp\left[-i\frac{\dot{\Omega}}{2}\left(\tau_3+\frac{\varpi(\vec{p}_2,\vec{q}_2)}{\dot{\Omega}}\right)^2\right]\exp\left[i\frac{\dot{\Omega}}{2}\left(\tau_4+\frac{\varpi(\vec{p}_2,\vec{q}_2)}{\dot{\Omega}}\right)^2\right] \\
&= \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4\left(\frac{2\pi}{\dot{\Omega}}\right)^2\sum_{\vec{p}_1,\vec{q}_1}^{<}\sum_{\vec{p}_2,\vec{q}_2}^{<}\delta\left(\vec{p}_1+\vec{q}_1,\vec{p}_2+\vec{q}_2\right).
\end{aligned}
$$

Upon collecting the results above, the contribution from the (D2) diagrams is

given by

$$
\begin{aligned}
A &= \sum_{j=1}^{5} A_j = \frac{1}{2} \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \left(\frac{2\pi}{\dot\Omega}\right)^2 \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2,\vec{q}_2}^{<} \delta\left(\vec{p}_1 + \vec{q}_1, \vec{p}_2 + \vec{q}_2\right) \\
&= \frac{N_0}{2} \times \frac{17}{105} \left(2\pi \frac{g^2}{\hbar^2\dot\Omega} \frac{n_0}{2}\right)^2 .
\end{aligned}
\tag{3.16}
$$

Each of the diagrams (D3) and (D4) contributes equally as

$$
\begin{aligned}
B &\equiv \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\gamma_2,\gamma_3=\pm} (\gamma_2\gamma_3) \sum_{\vec{p}_1,\vec{q}_1} \sum_{\vec{p}_2} \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \\
&\quad \times i\mathcal{F}_0^{++}\left(\vec{p}_1 + \vec{q}_1; \infty, \tau_1\right) i\mathcal{F}_0^{\gamma_2\gamma_3}\left(\vec{p}_2 + \vec{q}_1; \tau_2, \tau_3\right) i\mathcal{F}_0^{--}\left(\vec{p}_1 + \vec{q}_1; \tau_4, \infty\right) \\
&\quad \times i\mathcal{B}_0^{+\gamma_2}\left(\vec{q}_1; \tau_1, \tau_2\right) i\mathcal{B}_0^{\gamma_3 -}\left(\vec{q}_1; \tau_3, \tau_4\right) \\
&\quad \times i\mathcal{A}_0^{+-}\left(\vec{p}_1; \tau_1, \tau_4\right) i\mathcal{A}_0^{\gamma_3\gamma_2}\left(\vec{p}_2; \tau_3, \tau_2\right) = \sum_{j=1}^{5} B_j .
\end{aligned}
$$

The term B_1 is given by

$$
\begin{aligned}
B_1 &\equiv \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1} \sum_{\vec{p}_2} \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \, \theta\left(\tau_2 - \tau_3\right) \theta\left(\tau_1 - \tau_2\right) \\
&\quad \times i\mathcal{F}_0^{-+}\left(\vec{p}_1 + \vec{q}_1; \tau_4, \tau_1\right) i\mathcal{F}_0^{-+}\left(\vec{p}_2 + \vec{q}_1; \tau_2, \tau_3\right) \\
&\quad \times i\mathcal{B}_0^{-+}\left(\vec{q}_1; \tau_1, \tau_2\right) i\mathcal{B}_0^{+-}\left(\vec{q}_1; \tau_3, \tau_4\right) \\
&\quad \times i\mathcal{A}_0^{+-}\left(\vec{p}_1; \tau_1, \tau_4\right) i\mathcal{A}_0^{+-}\left(\vec{p}_2; \tau_3, \tau_2\right) = 0,
\end{aligned}
$$

since $\sum_{\vec{q}_1} \mathcal{B}_0^{-+}\left(\vec{q}_1; \tau_1, \tau_2\right) \mathcal{B}_0^{+-}\left(\vec{q}_1; \tau_3, \tau_4\right) = 0$.

The term B_2 is given by

$$
\begin{aligned}
B_2 &\equiv \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1} \sum_{\vec{p}_2} \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \, \theta\left(\tau_3 - \tau_2\right) \theta\left(\tau_4 - \tau_3\right) \\
&\quad \times i\mathcal{F}_0^{-+}\left(\vec{p}_1 + \vec{q}_1; \tau_4, \tau_1\right) i\mathcal{F}_0^{-+}\left(\vec{p}_2 + \vec{q}_1; \tau_2, \tau_3\right) \\
&\quad \times i\mathcal{B}_0^{+-}\left(\vec{q}_1; \tau_1, \tau_2\right) i\mathcal{B}_0^{-+}\left(\vec{q}_1; \tau_3, \tau_4\right) \\
&\quad \times i\mathcal{A}_0^{+-}\left(\vec{p}_1; \tau_1, \tau_4\right) i\mathcal{A}_0^{+-}\left(\vec{p}_2; \tau_3, \tau_2\right) = 0,
\end{aligned}
$$

since $\sum_{\vec{q}_1} \mathcal{B}_0^{+-}(\vec{q}_1; \tau_1, \tau_2) \, \mathcal{B}_0^{-+}(\vec{q}_1; \tau_3, \tau_4) = 0$.

The term B_3 is given by

$$
\begin{aligned}
B_3 \;\equiv\; & \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2}^{<} \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \, \theta\left(\tau_2 - \tau_3\right) \theta\left(\tau_2 - \tau_1\right) \\
& \times \exp\left[\frac{i}{\hbar} \int_{\tau_3}^{\tau_2} \left[\varepsilon_a(\vec{p}_2, \tau) + \varepsilon_b(\vec{q}_1, \tau) - \varepsilon_f(\vec{p}_2 + \vec{q}_1, \tau)\right] d\tau\right] \\
& \times \exp\left[\frac{i}{\hbar} \int_{\tau_1}^{\tau_4} \left[\varepsilon_a(\vec{p}_1, \tau) + \varepsilon_b(\vec{q}_1, \tau) - \varepsilon_f(\vec{p}_1 + \vec{q}_1, \tau)\right] d\tau\right]
\end{aligned}
$$

$$
\begin{aligned}
= \; & \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sqrt{\frac{2\pi}{-i\dot{\Omega}}} \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2}^{<} \int_{-\infty}^{+\infty} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \int_{-\infty}^{\tau_2} d\tau_3 \\
& \times \exp\left[-i\frac{\dot{\Omega}}{2}\left[\left(\tau_1 + \frac{\varpi(\vec{p}_1, \vec{q}_1)}{\dot{\Omega}}\right)^2 - \left(\tau_2 + \frac{\varpi(\vec{p}_2, \vec{q}_1)}{\dot{\Omega}}\right)^2 + \left(\tau_3 + \frac{\varpi(\vec{p}_2, \vec{q}_1)}{\dot{\Omega}}\right)^2\right]\right]
\end{aligned}
$$

$$
\begin{aligned}
= \; & \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sqrt{\frac{2\pi}{-i\dot{\Omega}}} \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2}^{<} \int_{-\infty}^{+\infty} dx \int_0^{\infty} dy \int_0^{\infty} dz \\
& \times \exp\left[-i\frac{\dot{\Omega}}{2}\left(x - y - z + \frac{\varpi(\vec{p}_1, \vec{q}_1)}{\dot{\Omega}}\right)^2\right] \exp\left[i\dot{\Omega}\left(y - \frac{\varpi(\vec{p}_1, \vec{q}_1) - \varpi(\vec{p}_2, \vec{q}_1)}{\dot{\Omega}}\right) z\right]
\end{aligned}
$$

$$
= \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \left(\frac{2\pi}{\dot{\Omega}}\right) \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2}^{<} \int_0^{\infty} dy \int_0^{\infty} dz \exp\left[i\dot{\Omega}\left(y - \frac{\varpi(\vec{p}_1, \vec{q}_1) - \varpi(\vec{p}_2, \vec{q}_1)}{\dot{\Omega}}\right) z\right],
$$

where the change of variables used is

$$
\begin{aligned}
\tau_2 &= x \in (-\infty, \infty), \\
\tau_1 &= x - y, \quad y \in [0, \infty), \\
\tau_3 &= x - z, \quad z \in [0, \infty).
\end{aligned}
$$

The term B_4 is given by

$$
\begin{aligned}
B_4 &\equiv \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1} \sum_{\vec{p}_2} \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \, \theta\left(\tau_3 - \tau_2\right) \theta\left(\tau_3 - \tau_4\right) \\
&\quad \times i\mathcal{F}_0^{-+}\left(\vec{p}_1 + \vec{q}_1; \tau_4, \tau_1\right) i\mathcal{F}_0^{-+}\left(\vec{p}_2 + \vec{q}_1; \tau_2, \tau_3\right) \\
&\quad \times i\mathcal{B}_0^{+-}\left(\vec{q}_1; \tau_1, \tau_2\right) i\mathcal{B}_0^{+-}\left(\vec{q}_1; \tau_3, \tau_4\right) \\
&\quad \times i\mathcal{A}_0^{+-}\left(\vec{p}_1; \tau_1, \tau_4\right) i\mathcal{A}_0^{+-}\left(\vec{p}_2; \tau_3, \tau_2\right)
\end{aligned}
$$

$$
\begin{aligned}
&= \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1} \sum_{\vec{p}_2} \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \, \theta\left(\tau_2 - \tau_3\right) \theta\left(\tau_2 - \tau_1\right) \\
&\quad \times \left(i\mathcal{F}_0^{-+}\left(\vec{p}_1 + \vec{q}_1; \tau_4, \tau_1\right)\right)^* \left(i\mathcal{F}_0^{-+}\left(\vec{p}_2 + \vec{q}_1; \tau_2, \tau_3\right)\right)^* \\
&\quad \times \left(i\mathcal{B}_0^{+-}\left(\vec{q}_1; \tau_1, \tau_2\right)\right)^* \left(i\mathcal{B}_0^{+-}\left(\vec{q}_1; \tau_3, \tau_4\right)\right)^* \\
&\quad \times \left(i\mathcal{A}_0^{+-}\left(\vec{p}_1; \tau_1, \tau_4\right)\right)^* \left(i\mathcal{A}_0^{+-}\left(\vec{p}_2; \tau_3, \tau_2\right)\right)^* .
\end{aligned}
$$

The sum $B_3 + B_4$ becomes

$$
\begin{aligned}
B_3 + B_4 &= \left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \left(\frac{2\pi}{\dot{\Omega}}\right) \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2}^{<} \\
&\quad \times \int_0^{\infty} dy \int_{-\infty}^{\infty} dz \, \exp\left[-i\dot{\Omega}\left(y - \frac{\varpi(\vec{p}_1,\vec{q}_1) - \varpi(\vec{p}_2,\vec{q}_1)}{\dot{\Omega}}\right) z\right]
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{2}\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \left(\frac{2\pi}{\dot{\Omega}}\right)^2 \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2}^{<} \\
&\quad \times \int_0^{\infty} \left[\delta\left(y - \frac{\varpi(\vec{p}_1,\vec{q}_1) - \varpi(\vec{p}_2,\vec{q}_1)}{\dot{\Omega}}\right) + \delta\left(y - \frac{\varpi(\vec{p}_2,\vec{q}_1) - \varpi(\vec{p}_1,\vec{q}_1)}{\dot{\Omega}}\right)\right] dy \\
&= \frac{1}{2}\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \left(\frac{2\pi}{\dot{\Omega}}\right)^2 \left(\frac{N_0}{2}\right)^3 .
\end{aligned}
$$

The term B_5 is given by

$$
\begin{aligned}
B_5 &\equiv (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \sum_{\vec{p}_1,\vec{q}_1}^{<} \sum_{\vec{p}_2}^{<} \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_4 \\
&\quad \times \exp\left[-i\frac{\dot{\Omega}}{2}\left(\tau_1 + \frac{\varpi(\vec{p}_1,\vec{q}_1)}{\dot{\Omega}}\right)^2\right] \exp\left[i\frac{\dot{\Omega}}{2}\left(\tau_4 + \frac{\varpi(\vec{p}_1,\vec{q}_1)}{\dot{\Omega}}\right)^2\right] \\
&\quad \times \exp\left[i\frac{\dot{\Omega}}{2}\left(\tau_2 + \frac{\varpi(\vec{p}_2,\vec{q}_1)}{\dot{\Omega}}\right)^2\right] \exp\left[-i\frac{\dot{\Omega}}{2}\left(\tau_3 + \frac{\varpi(\vec{p}_2,\vec{q}_1)}{\dot{\Omega}}\right)^2\right] \\
&= (-)\left(\frac{g}{\hbar\sqrt{\mathcal{V}}}\right)^4 \left(\frac{2\pi}{\dot{\Omega}}\right)^2 \left(\frac{N_0}{2}\right)^3.
\end{aligned}
$$

Upon collecting the results above, it is found that each of the diagrams (D3) and (D4) contributes equally as

$$
B = \sum_{j=1}^{5} B_j = -\frac{N_0}{2} \times \frac{1}{2}\left(2\pi \frac{g^2}{\hbar^2\dot{\Omega}}\frac{n_0}{2}\right)^2. \tag{3.17}
$$

Using the results of Eqs. (3.15), (3.16) and (3.17), and introducing the notation $\Gamma \equiv 2\pi\xi_{LZ}\left(\mathcal{V}\frac{n_0}{2}\right)$, where $\xi_{LZ} = \frac{g^2}{\mathcal{V}\hbar^2\dot{\Omega}}$ is the canonical LZ parameter [46, 47], one obtains

$$
\text{MCE} = \frac{2\left\langle \hat{N}_f \right\rangle(\infty)}{N_0} = \Gamma - \frac{88}{105}\Gamma^2 + \mathcal{O}\left(\Gamma^3\right), \tag{3.18}
$$

where the n-th term of this series is represented by the set of Feynman-Keldysh diagrams containing $2n$ vertices.

Eq.(3.18) reveals deviations from the universal two-level LZ formula (see Eq.(2.14) of Chapter II), and also from the phenomenological correction proposed in [51, 52] as

$$
\eta\left(1 - e^{-\Gamma}\right) = \eta\left(\Gamma - \frac{1}{2}\Gamma^2 + \mathcal{O}\left(\Gamma^3\right)\right), \tag{3.19}
$$

where $\eta \leq 50\%$ is a constant that depends only on the initial population of each of the two hyperfine states in the Fermi gas.

Since $\frac{88}{105} > \frac{1}{2}$, Eq.(3.18) shows that, as $\dot{B}^{-1}$ increases, the MCE grows slower

then predicted by the LZ formula, and this behavior is experimentally supported [16, 17, 18, 21]. The approach towards saturation is not due to a mere contraction of the LZ formula by a multiplicative factor determined solely by the initial state preparation, as proposed in the LZ scenarios [51, 52], but has a rather dynamical nature as the atom-molecule conversion takes place in a many-body medium in which the effects of quantum statistics play a crucial role.

Examination of higher order diagrams indicates that MCE is a function depending solely on the parameter Γ. Therefore, in the extreme adiabatic regime, corresponding to $\Gamma \to \infty$, MCE must have a universal limit at $T = 0$ which, unlike in the phenomenological result (3.19), is not a priori bounded by 50%. In practice, as the experiments are carried out at finite T and Γ, the smearing of the Fermi surface when T approaches T_F, and the quantum degeneracy reaches its lower limit, must be taken into account for analyzing the T-dependence of the MCE saturation [21].

CHAPTER IV

SUMMARY AND CONCLUSIONS

In Chapter II, I have given a complete and rigorous proof of the conjecture put forth by Brundobler and Elser [S. Brundobler and V. Elser, J. Phys. A **26**, 1211 (1993)], regarding the survival probability on the diabatic levels with maximum/minimum slope in a general N-state Landau-Zener (LZ) system.

In Chapter III, I have analyzed the molecular conversion efficiency (MCE) for a hyperfine-induced s-wave Feshbach resonance in an ultra-degenerate two-component atomic Fermi gas. In connection to this, I developed a consistent many-body nonequilibrium theory, based on the real-time Green function approach, in which all atomic and molecular states are included, and the effects of quantum statistics are fully accounted for. This theory can be readily generalized to include temperature effects and BCS-type correlations.

I demonstrated, by analytically evaluating the MCE up to fourth order in the hyperfine coupling constant, that the canonical LZ formula at two-level crossing is violated in this system due to many-body effects which systematically decrease the LZ transition probability, even for moderately small values of the inverse sweeping rate of the magnetic field. This result indicates that in degenerate Fermi gases the effects of quantum statistics near a Feshbach resonance play a crucial role, and the singling out of independent two-atom pairs from an ensemble of delocalized indistinguishable particles, as proposed in the LZ scenarios [51, 52], is untenable.

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