ABSTRACT

Basing on the first principles of Quantum mechanics as exposed in the previous chapters and sections, special chapters of quantum theory are here unfolded in order to further extend and caching the quantum information from free to observed evolution within the matter systems with constraints (boundaries). As such, the Feynman path integral formalism is firstly exposed and then applied to atomic, quantum barrier and quantum harmonically vibration, followed by density matrix approach, opening the Hartree-Fock and Density Functional pictures of many-electronic systems, with a worthy perspective of electronic occupancies via Koopmans theorem, while ending with a further generalization of the Heisenberg observability and of its first application to mesosystems.

4.1 INTRODUCTION

Not necessarily in an historical order but rather as a phenomenological classification, one should learn that the actual quantum chemistry originates in five levels of quantum approximations imposed on the many-electronic-many-nuclei systems, either in isolate or interacting state. They are summarized below along mentioning the current limitations, controversies and prospects.

1. *The Born-Oppenheimer approximation* (Born & Oppenheimer, 1927), while intended in producing a simplification of the electronic calculus for frozen nuclei approximation, breaks down actually when, for instance, computing the magnetic dipole moment and its derivative with respect to the nuclear velocities

or momenta, for assessing the molecular properties of surfaces (Buckingham et al., 1987).

2. *The single Slater determinant representation of the ground electronic state* (Slater, 1929), which nicely solved the exchange behavior of electrons by incorporating the Pauli repulsion in antisymmetric determinants (Pauli, 1940), was conceptually extended to the configuration interaction by the seminal works of Lowdin (Löwdin, 1955), while noting afterwards further generalization by the fruitful notion of the so-called complete active space (CAS) (Roos et al., 1980) that, when combined with other quantum chemical methods such as the self consistent field (SCF) and density functional theory (DFT) – see below, become very productive in accounting for *all* electronic states which contribute to the *reactive* space, be it which electronic states of species (reactants, intermediates and products) are involved in chemical reactions, thermally or photo-induced ones (Roos et al., 1982; Roos & Malmqvist, 2004).
3. *Simple Hückel* (Hückel, 1931) *and molecular orbitals' theories* (Parr et al., 1950; Roothaan, 1951, 1958; Purvis & Bartlett, 1982; Roothaan & Detrich, 1983; Pople et al., 1987; Curtiss et al., 1998; Ohlinger et al., 2009), nevertheless viewed as the next natural step over the paradigmatic Heitler-London theory of homopolar chemical bonding (Heitler & London, 1927), have been unlocking the door for self-consistent field Hartree-Fock-Slater theories (Pople & Nesbet, 1954; Roothaan, 1960; Corongiu, 2007; Glaesemann & Schmidt, 2010) and of associate semi-empirical formulations (Pariser & Parr, 1953; Pople, 1953) in treating a plethora of chemical system and phenomena on the base of their internal symmetry, while remarkably agreeing (and sometimes predicting) the observed spectra and reactivity, among which the pericyclic reactions (Beaudry et al., 2005; Hickenboth et al., 2007) and the Woodward-Hoffman rules (Woodward & Hoffmann, 1965; Hoffmann & Woodward, 1968) are eminent examples; yet, this direction let with the so-called quantum correlation problem (i.e., modeling the electronic movement in the dynamical field of the other electrons present in the system) that remains little tractable within the Slater (or even

with configurational interaction) framework; the solution in getting accurate correlations arrives with the advent of Density Functional Theory (DFT) and with the price of modifying the overall wave-function of the system and of its spectra.

4. *Thomas-Fermi theory* (Balàzs, 1967; Fermi, 1927; Lieb & Simon, 1977; Teller, 1962; Thomas, 1927) *along Walter Kohn's developments* (Hohenberg & Kohn, 1964; Kohn & Sham, 1965) *while* merging in the celebrated Density Functional Theory (Kohn et al., 1996) have the merit in being conceptually exact, i.e., performing the ab initio analysis of the electronic spectra relying only upon the universal constants of electronic charge, mass, Planck constant, and of their combinations in bare and effective potential, while providing an approximate set of orbitals (called as Kohn-Sham orbitals); they eventually correctly resemble the observed electronic density of the system along the measured energies (with correlation effects included), yet being with less significance even than the classical wave-function concept; actually, the current DFT uses as input the so-called basis function just like a mathematical tool, that can be adapted or optimized depending on the accuracy needed in relation with optimized effective potential (Bokhan & Bartlett, 2006), adding dispersion effects, etc. After all, the computationally implementation of DFT becomes so parameterized procedure that makes from it a sort of semi-empirical based DFT (Derosa, 2009), that can be nevertheless extended to include time-dependency excited states effects (Besley et al., 2009; Burke et al., 2005; Runge & Gross, 1984; March et al., 1999; Ploetner et al., 2010), as well as modeling the actual hot topic of Bose-Einstein condensates (Putz, 2011b). Moreover, it is worth saying that the great merit and paradox of DFT, is that the theory provides the recipe to compute two-body interactions (as exchange and correlations) by approximations to single body (density) behavior; from the physical point of view the picture is flawed, yet it turned out that the approximations works very well – markings therefore a landmark in quantum chemistry achievement; in passing this was perhaps also the reason the theory was Nobel awarded in Chemistry (in 1998) and not in Physics since there is no new physics inside but useful

reformulations (thus a new theory) for Chemistry. Recent works on DFT also try to further lighten on the DFT limits, i.e., formulating various approximations for exchange-correlation functionals (Putz, 2008) in more or less agreement with the fundamental theorems and limits at asymptotic and nuclei ranges (Capelle, 2006), until attempting to formulate expectation values of various physical observables based only on density similar to those based on the expectation value of quantum mechanical wave function (Bartlett & Musial, 2007), leads with the believe that true *ab initio DFT* is far for being fully engaged (Bartlett et al., 2004; Bartlett et al., 2005), while only *semi-empirical DFT* seems to prevail in a way or other when is about computational implementation. On the other side, still, the conceptual DFT (Geerlings et al., 2003), is of the first importance in formulating the chemical reactivity and its indices that help in understanding and modeling the chemical systems to a large extent (De Proft & Geerlings, 2001; Chermette, 1999).

5. *The solvent effects* seem to need almost always be taken into account when using quantum chemical treatment for describing chemical systems' reactivity. The environment interaction, and sometimes strongly interacting solvent molecules (e.g., water molecules in the case of biomolecules: amino acids, peptides, nucleic acids and their complexes) need to be considered in any modeling study of open chemical systems in order to fully understand and interpret the experimental results such as the vibrational, NMR and electronic spectra, and the chiral analogues (Tiwari et al., 2008). Overall, the interaction of the system with environment stands also in the foreground of the quantum theory when always predicting an additional quantum fluctuation upon the concerned system due to its coupling with the media/observer/solvent (Corni et al., 2003; Fung et al., 2006); it can be nevertheless implemented by counting for additional reactions and stability of the investigated chemical systems, while having also at side the quantum statistical tools for treating the macro-canonical samples in a correct physical way; worth saying that at this point DFT is well equipped from its basic definition of density - associated with the total number of electrons in the system - that can be then easily extended to

include also those effects coming from the environment (Nandini & Sathyanarayana, 2003).

6. *The density matrix theory*, the ancestor of density functional theory, provides the immediate framework for Path Integral (PI) development, allowing the canonical density be extended for the many-electronic systems through the density functional closure relationship. Yet, the use of path integral formalism for electronic density prescription presents several advantages: assures the inner quantum mechanical description of the system by parameterized paths; averages the quantum fluctuations; behaves as the propagator for time-space evolution of quantum information; resembles Schrödinger equation; allows quantum statistical description of the system through partition function computing. In this framework, four levels of path integral formalism can be approached: (1i) the Feynman quantum mechanical (present Chapter); (2i) the semiclassical, (3i) the Feynman-Kleinert effective classical, and the (4i) Fokker-Planck non-equilibrium ones (for the last three levels see Volume II of the present five-volume book). They lead with the practical specializations for quantum free and harmonic motions, for statistical high and low temperature limits, the smearing justification for the Bohr's quantum stability postulate with the paradigmatic Hydrogen atomic excursion, along the quantum chemical calculation of semiclassical electronegativity and hardness, of chemical action and Mulliken electronegativity, as well as by the Markovian generalizations of Becke-Edgecombe electronic focalization functions – all advocate for the reliability of assuming PI formalism of quantum mechanics as a versatile one, suited for analytically and/or computationally modeling of a variety of fundamental physical and chemical reactivity concepts characterizing the (density driving) many-electronic systems.

Accordingly, the present chapter combines these issues in a first systematical inside look on quantum chemistry by quantum mechanics, so planting the "seeds" for the next applications on atoms, molecules, nanostructures and bio-chemical interactions (see the next Volumes II–V of the present five-volume book).

4.2 FEYNMAN'S PATH INTEGRAL QUANTUM FORMALISM

4.2.1 CONSTRUCTION OF PATH INTEGRAL

One starts considering the slicing for the time interval $[t_b, t_a]$

$$t_b = t_{n+1} > t_n > ... > t_2 > t_1 > t_0 = t_a \tag{4.1}$$

with the spatial ending points recalled as $x' = x_b, x = x_a$ for the quantum propagator (Green function) of Chapters 2 and 3, see for instance Eq. (3.310) as the actual space-time evolution amplitude

$$(x_b t_b; x_a t_a) = \langle x_b | \exp\left(-\frac{i}{\hbar}(t_b - t_a)\widehat{H}\right) | x_a \rangle \tag{4.2}$$

may be firstly rewritten in terms of associate evolution operator

$$\widehat{U}(t_b - t_a) = \exp\left(-\frac{i}{\hbar}(t_b - t_a)\widehat{H}\right) \tag{4.3}$$

to successively become

$$\begin{aligned}(x_b t_b; x_a t_a) &= \langle x_b | \widehat{U}(t_b - t_a) | x_a \rangle \\ &= \langle x_b | \widehat{U}(t_b, t_n)\widehat{U}(t_n, t_{n-1})...\widehat{U}(t_j, t_{j-1})...\widehat{U}(t_2, t_1)\widehat{U}(t_1, t_a) | x_a \rangle \\ &= \prod_{j=1}^{n}\left[\int_{-\infty}^{+\infty} dx_j\right]\prod_{j=1}^{n+1}(x_j t_j; x_{j-1} t_{j-1})\end{aligned} \tag{4.4}$$

when *n*-times the complete eigen-coordinate set

$$\hat{1} = \int_{-\infty}^{+\infty} |x_j\rangle\langle x_j| dx_j, \; j = \overline{1,n} \tag{4.5}$$

was introduced for each pair of events, with the elementary propagator between them:

$$(x_j t_j; x_{j-1} t_{j-1}) = \langle x_j | \exp\left(-\frac{i}{\hbar}(t_j - t_{j-1})\widehat{H}\right) | x_{j-1} \rangle = \langle x_j | \exp\left(-\frac{i}{\hbar}\varepsilon\widehat{H}\right) | x_{j-1} \rangle \tag{4.6}$$

where the elementary time interval was set as

$$\varepsilon = t_j - t_{j-1} = \frac{t_b - t_a}{n+1} > 0 \tag{4.7}$$

Now, the elementary quantum evolution amplitude (4.7) is to be evaluated, firstly by reconsidering the eigen-coordinate unitary operator, in the working form

$$\hat{1}_x = \int_{-\infty}^{+\infty} |x\rangle\langle x| dx \tag{4.8}$$

to separate the operatorial Hamiltonian contributions to the kinetic and potential ones,

$$\widehat{H} = \widehat{T} + \widehat{V} \tag{4.9}$$

as:

$$\begin{aligned}\left(x_j t_j; x_{j-1} t_{j-1}\right) &\cong \left\langle x_j \left| e^{-\frac{i}{\hbar}\varepsilon \hat{V}\left(\hat{x},t_j\right)} \hat{1}_x e^{-\frac{i}{\hbar}\varepsilon \hat{T}\left(\hat{p},t_j\right)} \right| x_{j-1} \right\rangle \\ &= \int_{-\infty}^{+\infty} \left\langle x_j \left| e^{-\frac{i}{\hbar}\varepsilon \hat{V}\left(\hat{x},t_j\right)} \right| x \right\rangle \left\langle x \left| e^{-\frac{i}{\hbar}\varepsilon \hat{T}\left(\hat{p},t_j\right)} \right| x_{j-1} \right\rangle dx \end{aligned} \tag{4.10}$$

where we have used the first order limitation of the Baker-Hausdorff formula, see Eq. (2.347)

$$e^{-\frac{i}{\hbar}\varepsilon\left[\hat{V}\left(\hat{x},t_j\right)+\hat{T}\left(\hat{p},t_j\right)\right]} = e^{-\frac{i}{\hbar}\varepsilon \hat{V}\left(\hat{x},t_j\right)} e^{-\frac{i}{\hbar}\varepsilon \hat{T}\left(\hat{p},t_j\right)} + \underbrace{O\left(\varepsilon^2\right)}_{\cong 0} \tag{4.11}$$

that is we assumed the second order of elementary time intervals be vanishing

$$\varepsilon^2 \cong 0 \tag{4.12}$$

Next, each obtained working energetic contribution are evaluated separated as: for kinetic contribution the inserting of the momentum complete eigen-set

$$\hat{1}_{p_j} = \int_{-\infty}^{+\infty} |p_j\rangle\langle p_j| dp_j \tag{4.13}$$

yields:

$$\begin{aligned}\left\langle x\left|e^{-\frac{i}{\hbar}\varepsilon\hat{T}\left(\hat{p},t_j\right)}\right|x_{j-1}\right\rangle &= \int_{-\infty}^{+\infty}\left\langle x\left|e^{-\frac{i}{\hbar}\varepsilon\hat{T}\left(\hat{p},t_j\right)}\right|p_j\right\rangle\left\langle p_j\left|x_{j-1}\right.\right\rangle dp_j \\ &= \int_{-\infty}^{+\infty} e^{-\frac{i}{\hbar}\varepsilon T\left(p_j,t_j\right)}\underbrace{\left\langle x\left|p_j\right.\right\rangle}_{\frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}p_j x}}\underbrace{\left\langle p_j\left|x_{j-1}\right.\right\rangle}_{\frac{1}{\sqrt{2\pi\hbar}}e^{-\frac{i}{\hbar}p_j x_{j-1}}}dp_j \\ &= \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}p_j\left(x-x_{j-1}\right)}e^{-\frac{i}{\hbar}\varepsilon T\left(p_j,t_j\right)}\frac{dp_j}{2\pi\hbar}\end{aligned} \tag{4.14}$$

While for potential elementary amplitude we get:

$$\left\langle x_j\left|e^{-\frac{i}{\hbar}\varepsilon\hat{V}\left(\hat{x},t_j\right)}\right|x\right\rangle = e^{-\frac{i}{\hbar}\varepsilon V\left(x,t_j\right)}\underbrace{\left\langle x_j\left|x\right.\right\rangle}_{\delta\left(x_j-x\right)} = \delta\left(x_j-x\right)e^{-\frac{i}{\hbar}\varepsilon V\left(x,t_j\right)} \tag{4.15}$$

With relations (4.14) and (4.15) back in Eq. (4.11) the elementary propagator takes the form:

$$\begin{aligned}\left(x_j t_j; x_{j-1} t_{j-1}\right) &= \int_{-\infty}^{+\infty}\left(\int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}p_j\left(x-x_{j-1}\right)}e^{-\frac{i}{\hbar}\varepsilon T\left(p_j,t_j\right)}\frac{dp_j}{2\pi\hbar}\right)\left(\delta\left(x_j-x\right)e^{-\frac{i}{\hbar}\varepsilon V\left(x,t_j\right)}\right)dx \\ &= \int_{-\infty}^{+\infty}\frac{dp_j}{2\pi\hbar}\exp\left[\frac{ip_j\left(x_j-x_{j-1}\right)}{\hbar}-i\varepsilon\frac{T\left(p_j,t_j\right)+V\left(x_j,t_j\right)}{\hbar}\right] \\ &= \int_{-\infty}^{+\infty}\frac{dp_j}{2\pi\hbar}\exp\left\{\frac{i}{\hbar}\left[p_j\left(x_j-x_{j-1}\right)-\varepsilon H\left(x_j,p_j,t_j\right)\right]\right\}\end{aligned} \tag{4.16}$$

Replacing the elementary quantum amplitude (4.16) back in the global one given by Eq. (4.4), it assumes the form:

$$\begin{aligned}\left(x_b t_b; x_a t_a\right) &\cong \prod_{j=1}^{n}\left[\int_{-\infty}^{+\infty}dx_j\right]\prod_{j=1}^{n+1}\int_{-\infty}^{+\infty}\frac{dp_j}{2\pi\hbar}\exp\left\{\varepsilon\frac{i}{\hbar}\left[\begin{array}{l}p_j\dfrac{x_j-x_{j-1}}{\varepsilon} \\ -H\left(x_j,p_j,t_j\right)\end{array}\right]\right\} \\ &= \left(\prod_{j=1}^{n}\left[\int_{-\infty}^{+\infty}dx_j\right]\right)\left(\prod_{j=1}^{n+1}\left[\int_{-\infty}^{+\infty}\frac{dp_j}{2\pi\hbar}\right]\right)\exp\left\{\frac{i}{\hbar}\varepsilon\sum_{j=1}^{n+1}\left[\begin{array}{l}p_j\dfrac{x_j-x_{j-1}}{\varepsilon} \\ -H\left(x_j,p_j,t_j\right)\end{array}\right]\right\}\end{aligned} \tag{4.17}$$

which for in infinitesimal temporal partition,

$$n \to \infty; \varepsilon \to 0 \tag{4.18}$$

the quantum propagator behaves like the *Feynman path integral* (Dirac, 1933; Feynman, 1948; Wiener, 1923; Infeld & Hull, 1951; Schulmann, 1968; Abarbanel & Itzykson, 1969; Campbell et al., 1975; Laidlaw & DeWitt-Morette, 1971):

$$\left(x_b t_b; x_a t_a\right) \equiv \int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathsf{D}x\mathsf{D}p \exp\left\{\frac{i}{\hbar} S[x,p,t]\right\} \tag{4.19}$$

where we have considered the limiting notations for the path integral measure:

$$\lim_{n\to\infty}\left(\prod_{j=1}^{n}\left[\int_{-\infty}^{+\infty} dx_j\right]\right)\left(\prod_{j=1}^{n+1}\left[\int_{-\infty}^{+\infty} \frac{dp_j}{2\pi\hbar}\right]\right) \equiv \int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathsf{D}x\mathsf{D}p \tag{4.20}$$

and for the involved action:

$$\begin{aligned}\lim_{\substack{n\to\infty\\ \varepsilon\to 0}} \varepsilon \sum_{j=1}^{n+1}\left[p_j \frac{x_j - x_{j-1}}{\varepsilon} - H\left(x_j, p_j, t_j\right)\right] \\ \overset{(4.7)}{\equiv} \int_{t_a}^{t_b}\left[p(t)\dot{x}(t) - H\left(x(t), p(t), t\right)\right]dt = \int_{t_a}^{t_b} L\left(x(t), p(t), t\right)dt = S[x,p,t]\end{aligned} \tag{4.21}$$

Note that the results (4.19)–(4.21) account for quantum information for the quantum evolution of a system throughout accounting all histories (possibilities for linking two events in time-space) for a quantum evolution (Peak & Inomata, 1969; Gerry & Singh, 1979; Kleinert, 1989):

$$\left(x_b t_b; x_a t_a\right) = \sum_{\substack{ALL\\ HISTORIES}} \exp\left\{\frac{i}{\hbar} S[x,p,t]\right\} \tag{4.22}$$

thus being suitable to be implemented in the *N*-particle functional scheme once it is analytically computed (see the Section 4.3).

However, for achieving such goal, a more practical form of the Feynman integral may be obtained once the Hamiltonian is implemented as

$$H = \frac{p^2}{2m} + V(x,t) \tag{4.23}$$

leading with the action (4.21) unfolding

$$\begin{aligned} S[x,p,t] &= \sum_{j=1}^{n+1}\left[p_j\left(x_j - x_{j-1}\right) - \varepsilon\frac{p_j^2}{2m} - \varepsilon V(x_j,t_j)\right] \\ &= \sum_{j=1}^{n+1}\left[-\frac{\varepsilon}{2m}\left(p_j - \frac{x_j - x_{j-1}}{\varepsilon}m\right)^2 + \varepsilon\frac{m}{2}\left(\frac{x_j - x_{j-1}}{\varepsilon}\right)^2 - \varepsilon V(x_j,t_j)\right] \end{aligned} \tag{4.24}$$

allowing the momentum integrals in Eq. (4.20) to be solved out as

$$\int_{-\infty}^{+\infty}\frac{dp_j}{2\pi\hbar}\exp\left\{-\frac{i}{\hbar}\frac{\varepsilon}{2m}\left(p_j - \frac{x_j - x_{j-1}}{\varepsilon}m\right)^2\right\} = \sqrt{\frac{m}{2\pi\hbar i\varepsilon}} \tag{4.25}$$

through formally applying the Poisson formula (see Appendix A.1.2):

$$\int_{-\infty}^{+\infty}\exp\left(-ay^2\right)dy = \sqrt{\frac{\pi}{a}} \tag{4.26}$$

The remaining quantum evolution amplitude reads as the spatial path integral only:

$$\begin{aligned} \left(x_b t_b; x_a t_a\right) &= \left(\prod_{j=1}^{n}\left[\int_{-\infty}^{+\infty} dx_j\right]\right)\left(\prod_{j=1}^{n+1}\left[\sqrt{\frac{m}{2\pi\hbar i\varepsilon}}\right]\right)\exp\left\{\frac{i}{\hbar}\sum_{j=1}^{n+1}\left[\begin{array}{l}\varepsilon\dfrac{m}{2}\left(\dfrac{x_j - x_{j-1}}{\varepsilon}\right)^2 \\ -\varepsilon V(x_j,t_j)\end{array}\right]\right\} \\ &= \frac{1}{\sqrt{2\pi\hbar i\varepsilon/m}}\prod_{j=1}^{n}\left[\int_{-\infty}^{+\infty}\frac{dx_j}{\sqrt{2\pi\hbar i\varepsilon/m}}\right]\exp\left\{\frac{i}{\hbar}\varepsilon\sum_{j=1}^{n+1}\left[\begin{array}{l}\dfrac{m}{2}\left(\dfrac{x_j - x_{j-1}}{\varepsilon}\right)^2 \\ -V(x_j,t_j)\end{array}\right]\right\} \\ &\underset{\varepsilon\to 0}{\overset{n\to\infty}{\to}}\int_{x(t_a)=x_a}^{x(t_b)=x_b}\mathsf{D}'x\exp\left\{\frac{i}{\hbar}S[x,\dot{x},t]\right\} \end{aligned} \tag{4.27}$$

with the actual modified measure of integration:

$$\int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathsf{D}'x \equiv \lim_{\substack{n\to\infty \\ \varepsilon\to 0}} \left(\frac{1}{\sqrt{2\pi\hbar i\varepsilon / m}} \prod_{j=1}^{n} \left[\int_{-\infty}^{+\infty} \frac{dx_j}{\sqrt{2\pi\hbar i\varepsilon / m}} \right] \right) \tag{4.28}$$

and the working action:

$$S[x,\dot{x},t] = \int_{t_a}^{t_b} L\left(x,\dot{x},t\right) dt = \int_{t_a}^{t_b} \left[\frac{m\dot{x}^2}{2} - V(x,t) \right] dt \tag{4.29}$$

Note that when the *partition function* is considered, another space coordinate is to be taken over the path integral (4.27), namely:

$$Z\left(t_b;t_a\right) = \int_{-\infty}^{+\infty} \left(xt_b;xt_a\right) dx = \int_{x(t_a)=x(t_b)} \mathsf{D}''x \exp\left\{ \frac{i}{\hbar} S[x,\dot{x},t] \right\} \tag{4.30}$$

while the new integration measure

$$\int_{x(t_a)=x(t_b)} \mathsf{D}''x \equiv \lim_{n\to\infty} \left(\prod_{j=1}^{n+1} \left[\int_{-\infty}^{+\infty} \frac{dx_j}{\sqrt{2\pi\hbar i\varepsilon / m}} \right] \right) \tag{4.31}$$

Ones of the main advantages dealing with path integrals relays on following:

- Attractive conceptual representation of dynamical quantum processes without operatorial excursion;
- Allows for quantum fluctuation description in analogy with thermal analogies,

$$\left(x_b t_b; x_a t_a\right)_{QM} = \int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathsf{D}'x(t) \exp\left\{ \frac{i}{\hbar} \int_{t_a}^{t_b} \left[\frac{m\dot{x}^2}{2} - V\left(x(t),t\right) \right] dt \right\} \tag{4.32}$$

through changing the temporal intervals with the thermodynamic temperature (T) by means of Wick transformation

$$\begin{cases} t := -i\tau, \ \tau = \hbar\beta, \beta = \dfrac{1}{k_B T} \\ dt = -id\tau \\ \dfrac{d}{dt} = i\dfrac{d}{d\tau} \end{cases} \tag{4.33}$$

i.e. transforming quantum mechanical (QM) into quantum statistical (QS) propagators:

$$\left(x_b\hbar\beta;x_a 0\right)_{QS}=\int\limits_{x(0)=x_a}^{x(\hbar\beta)=x_b}\mathsf{D}'x(\tau)\exp\left\{-\frac{1}{\hbar}\int\limits_0^{\hbar\beta}\left[\begin{matrix}\frac{m}{2}\dot{x}^2(\tau)\\+V\left(x(\tau),\tau\right)\end{matrix}\right]d\tau\right\} \tag{4.34}$$

from where immediately writing also the associate QS-partition function:

$$\begin{aligned}Z_{QS}\left(\beta\right)&=\int\limits_{-\infty}^{+\infty}\left(x_b\hbar\beta;x_a 0\right)_{QS}\,dx\\&=\int\limits_{x(0)=x(\hbar\beta)}\mathsf{D}''x\exp\left\{-\frac{1}{\hbar}\int\limits_0^{\hbar\beta}L^{+}\left(x,\dot{x},\tau\right)d\tau\right\}\end{aligned} \tag{4.35}$$

both QS object having the effect of transforming the *canonical Lagrangian* of action into the so-called *Euclidian* one

$$L^{+}\left(x,\dot{x},\tau\right)=\frac{m}{2}\dot{x}^2(\tau)+V\left(x(\tau),\tau\right) \tag{4.36}$$

analogous with the fact the Euclidian metric has all its diagonal terms as with positive sign.

Yet, the connection of the path integrals of propagators with the Schrödinger quantum formalism is to be revealed, and in next addressed.

4.2.2 PROPAGATOR'S EQUATION

There are two ways for showing the propagator path integral links with Schrödinger equation.

Firstly, there is by employing one of the above path integral, say that of Eq. (4.27) with Eq. (4.29),

$$\left(x_b t_b;x_a t_a\right)=\int\limits_{x(t_a)=x_a}^{x(t_b)=x_b}\mathsf{D}'x\exp\left\{\frac{i}{\hbar}S[x,\dot{x},t]\right\} \tag{4.37}$$

to perform the derivative:

$$\frac{\partial}{\partial x_b}\left(x_b,t_b;x_a,t_a\right)=\frac{\left(x_b+\delta x(t_b),t_b;x_a,t_a\right)-\left(x_b,t_b;x_a,t_a\right)}{\delta x(t_b)}$$

$$=\frac{1}{\delta x(t_b)}\left[\begin{array}{l}\displaystyle\int_{x(t_a)=x_a}^{x(t_b)=x_b}\mathsf{D}'x\exp\left\{\begin{array}{l}\dfrac{i}{\hbar}S[x(t)\\+\delta x(t)]\end{array}\right\}\\[2ex]\displaystyle-\int_{x(t_a)=x_a}^{x(t_b)=x_b}\mathsf{D}'x\exp\left\{\frac{i}{\hbar}S[x(t)]\right\}\end{array}\right]$$

$$=\frac{1}{\delta x(t_b)}\delta S\frac{\displaystyle\int_{x(t_a)=x_a}^{x(t_b)=x_b}\mathsf{D}'x\exp\left\{\begin{array}{l}\dfrac{i}{\hbar}S[x(t)\\+\delta x(t)]\end{array}\right\}-\int_{x(t_a)=x_a}^{x(t_b)=x_b}\mathsf{D}'x\exp\left\{\frac{i}{\hbar}S[x(t)]\right\}}{\delta S}$$

$$=\frac{1}{\delta x(t_b)}\delta S\frac{\delta\left(x_b,t_b;x_a,t_a\right)}{\delta S}$$

$$=\frac{1}{\delta x(t_b)}\delta S\frac{i}{\hbar}\left(x_b,t_b;x_a,t_a\right)$$

$$=\frac{1}{\delta x(t_b)}\left[\int_{t_a}^{t_b}\left(\frac{\partial L}{\partial x}\delta x+\frac{\partial L}{\partial\dot{x}}\delta\dot{x}\right)dt\right]\frac{i}{\hbar}\left(x_b,t_b;x_a,t_a\right)$$

$$=\frac{1}{\delta x(t_b)}\left[\int_{t_a}^{t_b}\left(\frac{\partial L}{\partial x}\delta x+\frac{\partial L}{\partial\dot{x}}\frac{d}{dt}\delta x\right)dt\right]\frac{i}{\hbar}\left(x_b,t_b;x_a,t_a\right)$$

$$=\frac{1}{\delta x(t_b)}\left[\begin{array}{l}\dfrac{\partial L}{\partial\dot{x}}\dfrac{\partial}{\partial t}\delta x\Big|_{t_a}^{t_b}\\[2ex]\displaystyle+\int_{t_a}^{t_b}\underbrace{\left(\frac{\partial L}{\partial x}-\frac{d}{dt}\frac{\partial L}{\partial\dot{x}}\right)}_{=0}\delta x dt\\[2ex]\qquad Euler-Lagrange\ \ equation\end{array}\right]\frac{i}{\hbar}\left(x_b,t_b;x_a,t_a\right)$$

$$= \frac{1}{\delta x(t_b)}\left[\frac{\partial L}{\partial \dot{x}}(t_b)\frac{\partial}{\partial t}\underbrace{\delta x(t_b)}_{\neq 0} - \frac{\partial L}{\partial \dot{x}}(t_a)\frac{\partial}{\partial t}\underbrace{\delta x(t_a)}_{=0}\right]\frac{i}{\hbar}\left(x_b,t_b;x_a,t_a\right)$$

$$= \underbrace{\frac{\partial L}{\partial \dot{x}}(t_b)}_{p(t_b)}\frac{i}{\hbar}\left(x_b,t_b;x_a,t_a\right);$$

$$\frac{\partial}{\partial x_b}\left(x_b,t_b;x_a,t_a\right) = \left[\frac{i}{\hbar}p(t_b)\right]\left(x_b,t_b;x_a,t_a\right) \tag{4.38}$$

Similarly for the second derivative we have:

$$\frac{\partial}{\partial x_b^2}\left(x_b,t_b;x_a,t_a\right) = \left[\frac{i}{\hbar}p(t_b)\right]^2\left(x_b,t_b;x_a,t_a\right) = -\frac{p^2(t_b)}{\hbar^2}\left(x_b,t_b;x_a,t_a\right) \tag{4.39}$$

while for time derivative we obtain following the same formal steps as before for coordinate derivatives:

$$\frac{\partial}{\partial t_b}\left(x_b,t_b;x_a,t_a\right) = \frac{\delta S}{\delta t_b}\frac{i}{\hbar}\left(x_b,t_b;x_a,t_a\right) = -\frac{i}{\hbar}H(t_b)\left(x_b,t_b;x_a,t_a\right) \tag{4.40}$$

by recalling the Hamilton-Jacobi equation of motion in the form

$$\frac{\delta S}{\delta t_b} = -H(t_b) \tag{4.41}$$

Now, there is immediate that for a Hamiltonian of the form (4.23) one gets through multiplying both its side with the propagator (4.37) and then considering for the square momentum and Hamiltonian terms the relations (4.39) and (4.41), respectively, one leaves with the Schrödinger type equation for the path integral:

$$i\hbar\frac{\partial}{\partial t_b}\left(x_b,t_b;x_a,t_a\right) = \left[-\frac{\hbar^2}{2m}\frac{\partial}{\partial x_b^2} + V(x_b)\right]\left(x_b,t_b;x_a,t_a\right) \tag{4.42}$$

Remarkably, besides establishing the link with the Schrödinger picture, Eq. (4.42) tells something more important, namely that the wave function itself, i.e., $\Psi\left(x_b,t_b\right)$ that usually fulfills equations like Eq. (4.42) may be replaced (and generalized as well) by the quantum propagator $\left(x_b,t_b;x_a,t_a\right)$ with the crucial consequence in that the propagator is providing the *N*-electronic density in the direct and elegant manner as

$$\rho_N\left(x;t_b-t_a\right)=\frac{N}{Z\left(t_b;t_a\right)}\left(x_b,t_b;x_a,t_a\right)\Big|_{x_b=x_b=x} \tag{4.43}$$

with partition function given as in (4.30), assuring for the correct *N*-representability (as is fundamental in density functional theory (DFT)) constraint:

$$\int \rho_N\left(x;t_b-t_a\right)dx=N \tag{4.44}$$

thus nicely replacing the complicated many-body wave function calculations.

Nevertheless, the path integral formalism is able to provide also *the exact* Schrödinger equation for the wave function, as will be shown in the sequel.

4.2.3 RECOVERING WAVE FUNCTION'S EQUATION

The starting point is the manifested *equivalence* between the path integral propagator and the Green function, with the role in transforming one wave-function registered on one space-time event into other one, either in the future or past quantum evolution. Here, we consider only retarded phenomena,

$$\left(x_2,t_2;x_1,t_1\right)=iG^{+}\left(x_2,t_2;x_1,t_1\right) \tag{4.45}$$

in accordance with the very beginning path integral construction, see the grid (4.1) and the relation (4.2), and consider the so-called quantum Huygens principle of wave-packet propagation (Greiner & Reinhardt, 1994):

$$\psi\left(x_2,t_2\right)=\int\left(x_2,t_2;x_1,t_1\right)\psi\left(x_1,t_1\right)dx_1\ ,\ t_2>t_1 \tag{4.46}$$

Yet, we will employ Eq. (4.46) for an *elementary* propagator, for a quantum evolution as presented in Figure 4.1, thus becoming like:

$$\psi\left(x,t+\varepsilon\right)=A\int\exp\left[\frac{i}{\hbar}\varepsilon L\left(\frac{x+x_0}{2},\frac{x-x_0}{2},t+\frac{\varepsilon}{2}\right)\right]\psi\left(x-\xi,t\right)dx_0 \tag{4.47}$$

where *A* plays the role of the normalization constant in Eq. (4.47) to assure the convergence of the wave function result. Equation (4.47) may be still transformed through employing the geometrical relation:

$$x=x_0+\xi \tag{4.48}$$

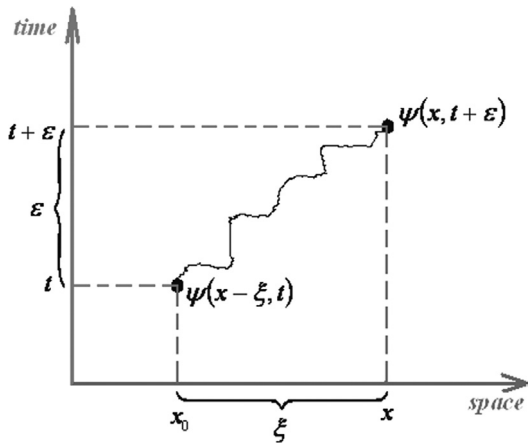

FIGURE 4.1 Depiction of the space-time elementary retarded path connecting two events characterized by their dynamic wave-functions.

to compute the space and velocity averages:

$$\frac{x+x_0}{2}=\frac{2x-\xi}{2}=x-\frac{\xi}{2} \tag{4.49}$$

$$\frac{x-x_0}{\varepsilon}=\frac{\xi}{\varepsilon} \tag{4.50}$$

respectively, while changing the variable

$$dx_0=-d\xi \tag{4.51}$$

to the actual form:

$$\psi\left(x,t+\varepsilon\right)=\tilde{A}\int\exp\left\{\frac{i}{\hbar}\varepsilon\left[\begin{array}{l}\dfrac{m}{2}\dfrac{\xi^2}{\varepsilon^2}\\ -V\left(x-\dfrac{\xi}{2},t+\dfrac{\varepsilon}{2}\right)\end{array}\right]\right\}\psi\left(x-\xi,t\right)d\xi$$

$$=\tilde{A}\int\exp\left[\frac{im}{2\hbar\varepsilon}\xi^2\right]\exp\left[-\frac{i}{\hbar}\varepsilon V\left(\begin{array}{l}x-\dfrac{\xi}{2},t\\ +\dfrac{\varepsilon}{2}\end{array}\right)\right]\psi\left(x-\xi,t\right)d\xi \tag{4.52}$$

where Lagrangian was considered with its canonical form, as in Eq. (4.29), and the new constant factor was considered assimilating the minus sign of (4.52).

Next, since noticing the square dependence of ξ in Eq. (4.52) there will be assumed the series expansion in coordinate (ξ) and time (ε) elementary steps restrained to the second and first order, respectively, being the time interval cut-off in accordance with the general (4.12) prescription. Thus we have:

$$\psi\left(x-\xi,t\right)\cong\psi\left(x,t\right)-\xi\left[\frac{\partial}{\partial x}\psi\left(x,t\right)\right]_{\xi\to 0}+\frac{\xi^2}{2}\left[\frac{\partial^2}{\partial x^2}\psi\left(x,t\right)\right]_{\xi\to\mathbf{0}} \tag{4.53}$$

$$\psi\left(x,t+\varepsilon\right)\cong\psi\left(x,t\right)+\varepsilon\left[\frac{\partial}{\partial t}\psi\left(x,t\right)\right]_{\varepsilon\to 0} \tag{4.54}$$

$$\exp\left[-\frac{i}{\hbar}\varepsilon V\left(x-\frac{\xi}{2},t+\frac{\varepsilon}{2}\right)\right]\cong 1-\frac{i}{\hbar}\varepsilon V\left(x,t\right) \tag{4.55}$$

and the form Eq. (4.52) successively rearranges:

$$\begin{aligned}
&\psi\left(x,t\right)+\varepsilon\left[\frac{\partial}{\partial t}\psi\left(x,t\right)\right]\\
&=\tilde{A}\int e^{-\frac{m}{2i\hbar\varepsilon}\xi^2}\left[1-\frac{i}{\hbar}\varepsilon V\left(x,t\right)\right]\left\{\begin{array}{l}\psi\left(x,t\right)\\-\xi\left[\dfrac{\partial}{\partial x}\psi\left(x,t\right)\right]\\+\dfrac{\xi^2}{2}\left[\dfrac{\partial^2}{\partial x^2}\psi\left(x,t\right)\right]\end{array}\right\}d\xi\\
&=\tilde{A}\psi\left(x,t\right)\int e^{-\frac{m}{2i\hbar\varepsilon}\xi^2}d\xi-\tilde{A}\left[\frac{\partial}{\partial x}\psi\left(x,t\right)\right]\int\xi e^{-\frac{m}{2i\hbar\varepsilon}\xi^2}d\xi\\
&\qquad+\tilde{A}\frac{1}{2}\left[\frac{\partial^2}{\partial x^2}\psi\left(x,t\right)\right]\int\xi^2 e^{-\frac{m}{2i\hbar\varepsilon}\xi^2}d\xi\\
&-\tilde{A}\frac{i}{\hbar}\varepsilon V\left(x,t\right)\psi\left(x,t\right)\int e^{-\frac{m}{2i\hbar\varepsilon}\xi^2}d\xi\\
&+\tilde{A}\frac{i}{\hbar}\varepsilon V\left(x,t\right)\left[\frac{\partial}{\partial x}\psi\left(x,t\right)\right]\int\xi e^{-\frac{m}{2i\hbar\varepsilon}\xi^2}d\xi
\end{aligned} \tag{4.56}$$

where we have neglected the mixed orders producing a total order beyond maximum two, for example, $\varepsilon\xi^2\cong 0$, and were we arranged the exponentials under integrals such that be of Gaussian type (i.e., employing

the identity $-i=1/i$). Now, the integrals appearing on Eq. (4.56) are of Poisson type of various orders, and solves for notation

$$\frac{m}{2\hbar\varepsilon i}\equiv a \tag{4.57}$$

as:

$$\int e^{-\frac{m}{2i\hbar\varepsilon}\xi^2}d\xi\to\int_{-\infty}^{+\infty}\exp\left(-a\xi^2\right)d\xi=\sqrt{\frac{\pi}{a}}=\sqrt{\frac{2\pi\hbar\varepsilon i}{m}} \tag{4.58}$$

$$\int \xi e^{-\frac{m}{2i\hbar\varepsilon}\xi^2}d\xi\to\int_{-\infty}^{+\infty}\xi\exp\left(-a\xi^2\right)d\xi=0 \tag{4.59}$$

$$\int \xi^2 e^{-\frac{m}{2i\hbar\varepsilon}\xi^2}d\xi\to\int_{-\infty}^{+\infty}\xi^2\exp\left(-a\xi^2\right)d\xi=\frac{1}{2a}\sqrt{\frac{\pi}{a}}=\frac{\hbar\varepsilon i}{m}\sqrt{\frac{2\pi\hbar\varepsilon i}{m}} \tag{4.60}$$

With these the expression (4.56) simplifies to:

$$\psi\left(x,t\right)+\varepsilon\left[\frac{\partial}{\partial t}\psi\left(x,t\right)\right]=\tilde{A}\sqrt{\frac{2\pi\hbar\varepsilon i}{m}}\left[\begin{matrix}1+\frac{1}{2}\frac{\hbar\varepsilon i}{m}\frac{\partial^2}{\partial x^2}\\-\frac{i}{\hbar}\varepsilon V\left(x,t\right)\end{matrix}\right]\psi\left(x,t\right) \tag{4.61}$$

which in the limit $\varepsilon\to 0$, common for path integrals, leaves with identity:

$$\psi\left(x,t\right)=\lim_{\varepsilon\to 0}\left(\tilde{A}\sqrt{\frac{2\pi\hbar\varepsilon i}{m}}\right)\psi\left(x,t\right) \tag{4.62}$$

from where the convergence constant of path integral (4.52) is found

$$\tilde{A}\left(\varepsilon\right)=\sqrt{\frac{m}{2\pi\hbar\varepsilon i}} \tag{4.63}$$

with identical form as previously, see Eq. (4.25), thus confirming the consistency of the present approach. Nevertheless, with the constant (4.63) back in Eq. (4.61) we get the equivalent forms:

$$\begin{aligned}\psi\left(x,t\right)+\varepsilon\left[\frac{\partial}{\partial t}\psi\left(x,t\right)\right]&=\psi\left(x,t\right)+\frac{1}{2}\frac{\hbar\varepsilon i}{m}\frac{\partial^2}{\partial x^2}\psi\left(x,t\right)-\frac{i}{\hbar}\varepsilon V\left(x,t\right)\psi\left(x,t\right)\\&\Leftrightarrow\frac{\partial}{\partial t}\psi\left(x,t\right)=\frac{1}{2}\frac{\hbar i}{m}\frac{\partial^2}{\partial x^2}\psi\left(x,t\right)-\frac{i}{\hbar}V\left(x,t\right)\psi\left(x,t\right)\end{aligned}$$

$$\Leftrightarrow i\hbar\frac{\partial}{\partial t}\psi(x,t)=\left[-\frac{1}{2}\frac{\hbar^2}{m}\frac{\partial^2}{\partial x^2}+V(x,t)\right]\psi(x,t) \tag{4.64}$$

being this last one identically recovering the Schrödinger wave function equation.

There was therefore thoroughly proofed that the Feynman path integral is may be reduced to the quantum wave-packet motion while carrying also the information that connects coupled events across the paths' evolution, being in this a general approach of quantum mechanics and statistics.

Next section(s) will deal with presenting practical application/calculation of the path integrals for fundamental quantum systems, from free and harmonic oscillator motion to Bohr and quantum barrier too.

4.3 PATH INTEGRALS FOR BASIC MATTER'S STRUCTURES

4.3.1 GENERAL PATH INTEGRAL'S PROPERTIES

There are three fundamental properties most useful for path integral calculations (Dittrich & Reuter, 1994).

1. Firstly, one may combine the two above Schrödinger type information about path integrals: the fact that propagator itself $(x_b,t_b;x_a,t_a)$ obeys the Schrödinger equation, see Eq. (4.42), thus behaving as a sort of wave-function and the fact that Schrödinger equation of the wave-function is recovered by the quantum Huygens principle of wave-packet propagation, see Eq. (4.46). Thus it makes sense to rewrite Eq. (4.46) with the propagator instead of wave-function obtaining the so-called *group property for propagators*:

$$(x_3,t_3;x_1,t_1)=\int(x_3,t_3;x_2,t_2)(x_2,t_2;x_1,t_1)dx_2,\ t_3>t_2>t_1 \tag{4.65}$$

which, nevertheless, may be recursively applied until covering the entire time slicing of the interval $[t_a,t_b]$ as given in (4.1):

$$(x_b,t_b;x_a,t_a)=\int(x_b,t_b;x_n,t_n)(x_n,t_n;x_{n-1},t_{n-1})\cdots(x_1,t_1;x_a,t_a)\prod_{j=1}^{n}dx_j \tag{4.66}$$

while remarking the absence of time intermediate integration.

2. Secondly, from the Huygens principle Eq. (4.46) there is abstracted also the limiting delta Dirac-function for a propagator connecting two space events simultaneously:

$$\left(x,t_1;x_1,t_1\right)=\delta\left(x-x_1\right) \tag{4.67}$$

as immediately is checked out:

$$\psi\left(x,t_1\right)=\int\left(x,t_1;x_1,t_1\right)\psi\left(x_1,t_1\right)dx_1=\int\delta\left(x-x_1\right)\psi\left(x_1,t_1\right)dx_1 \tag{4.68}$$

This property is often used as the analytical check once a path integral propagator is calculated for a given system.

3. Thirdly, and perhaps most practically, one would like to be able to solve the path integrals, say with canonical Lagrangian form (4.32), in more direct way than to consider all multiple integrals involved in the measure (4.28).

Hopefully, this is possible working out the quantum fluctuations along the classical path connecting two space-time events. In other words, this is to disturb the classical path $x_{cl}(t)$ by the quantum fluctuations $\delta x(t)$ to obtain the quantum evolution path:

$$x(t)=x_{cl}(t)+\delta x(t) \tag{4.69}$$

and its first time derivation:

$$\dot{x}(t)=\dot{x}_{cl}(t)+\delta\dot{x}(t) \tag{4.70}$$

Very important, note that the quantum fluctuation vanishes at the endpoints of the evolution path since "meeting" with the classical (observed) path, see Figure 4.2:

$$\delta x(t_a)=0=\delta x(t_b) \tag{4.71}$$

being these known as the *Dirichlet boundary conditions*.

With these the purpose is to separate the classical by the quantum fluctuation contributions also in the path integral propagator. Fortunately this is possible for enough large class of potentials, more precisely for quadratic Lagrangian's of general type:

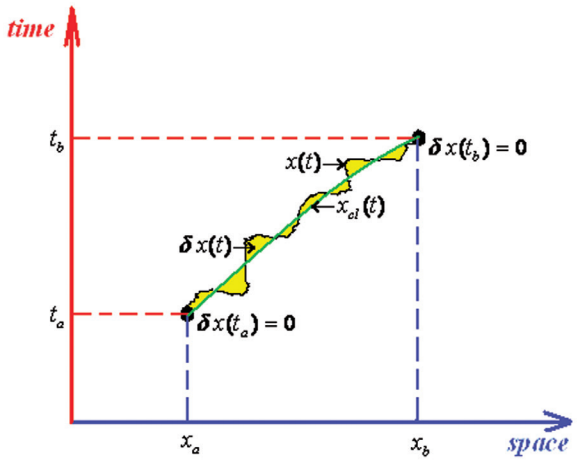

FIGURE 4.2 Illustration of the quantum fluctuations $\delta x(t)$ around the classical path $x_{cl}(t)$ producing the space-time evolution of the Figure 4.1.

$$L(x,\dot{x},t) = \alpha(t)x^2 + \beta(t)x\dot{x} + \gamma(t)\dot{x}^2 + \lambda(t)x + \chi(t)\dot{x} + \sigma(t) \qquad (4.72)$$

Expanding the path integral action (4.29) around the classical path requires the expansion of its associate Lagrangian (4.72); we get accordingly:

$$L(x,\dot{x},t) = L(x_{cl},\dot{x}_{cl},t) + \left[\frac{\partial L}{\partial x}\delta x + \frac{\partial L}{\partial \dot{x}}\delta\dot{x}\right]_{x_{cl},\dot{x}_{cl}} + \frac{1}{2}\left[\begin{array}{l}\dfrac{\partial^2 L}{\partial x^2}\delta x + 2\dfrac{\partial^2 L}{\partial x \partial \dot{x}}\delta x\delta\dot{x} \\ + \dfrac{\partial^2 L}{\partial \dot{x}^2}\delta\dot{x}^2\end{array}\right]_{x_{cl},\dot{x}_{cl}} \qquad (4.73)$$

$$\begin{aligned} S[x,\dot{x},t] &= \int_{t_a}^{t_b} L(x,\dot{x},t)\,dt \\ &= \int_{t_a}^{t_b} L(x_{cl},\dot{x}_{cl},t)\,dt + \int_{t_a}^{t_b}\left[\frac{\partial L}{\partial x}\delta x + \frac{\partial L}{\partial \dot{x}}\delta\dot{x}\right]_{x_{cl},\dot{x}_{cl}} dt \\ &\quad + \int_{t_a}^{t_b}\left[\alpha(t)\delta x + \beta(t)\delta x\delta\dot{x} + \gamma(t)\delta\dot{x}^2\right]dt \end{aligned}$$

$$= S_{cl}[x_{cl}, \dot{x}_{cl}, t] + \underbrace{\frac{\partial L}{\partial \dot{x}} \delta x \Big|_{t_a}^{t_b}}_{\substack{=0 \\ \delta x(t_a)=0=\delta x(t_b)}} + \int_{t_a}^{t_b} \underbrace{\left(\frac{\partial L}{\partial x} - \frac{d}{dt} \frac{\partial L}{\partial \dot{x}} \right)}_{\substack{=0 \\ Euler-Lagrange}} \delta x dt$$

$$+ \int_{t_a}^{t_b} \left[\alpha(t) \delta x + \beta(t) y \delta \dot{x} + \gamma(t) \delta \dot{x}^2 \right] dt$$

$$= S_{cl}[x_{cl}, \dot{x}_{cl}, t] + \int_{t_a}^{t_b} \left[\alpha(t) \delta x + \beta(t) y \delta \dot{x} + \gamma(t) \delta \dot{x}^2 \right] dt \tag{4.74}$$

With action (4.74) one observes it practically *separates* into the classical and quantum fluctuation contributions; this has two major consequences:

- The classical action goes outside of the path integration simply becoming the multiplication factor $\exp\left[(i/\hbar) S_{cl}\right]$;
- The remaining contribution since depending only on quantum fluctuation $\delta x(t)$ allow in the changing of integration measure:

$$\int_{x(t_a)=x_a}^{x(t_b)=x_b} \mathrm{D}' x(t) \to \int_{\delta x(t_a)=0}^{\delta x(t_b)=0} \underbrace{\left| \frac{\delta x(t)}{\delta(\delta x(t))} \right|}_{\substack{=1 \\ eq.\ (4.69)}} \mathrm{D}' \delta x(t) = \int_{\delta x(t_a)=0}^{\delta x(t_b)=0} \mathrm{D}' \delta x(t) \tag{4.75}$$

In these circumstances the path integral propagator factorizes as:

$$\left(x_b, t_b; x_a, t_a\right) = \underbrace{\exp\left\{ \frac{i}{\hbar} S_{cl}[x_{cl}, \dot{x}_{cl}, t] \right\}}_{\substack{classical \\ contribution}} \underbrace{\int_{\delta x(t_a)=0}^{\delta x(t_b)=0} \mathrm{D}' \delta x(t) \exp\left\{ \frac{i}{\hbar} \int_{t_a}^{t_b} \begin{bmatrix} \alpha(t) \delta x \\ + \beta(t) y \delta \dot{x} \\ + \gamma(t) \delta \dot{x}^2 \end{bmatrix} dt \right\}}_{quantum\ \ fluctuations} \tag{4.76}$$

Few conceptual comments are now compulsory based on the path integral form (4.76):

- There is clear that since the quantum fluctuation term does not depend on ending space coordinates but only on their time coordinates, so that in the end will depend only on the time difference $\left(t_b - t_a\right)$ since by means of energy conservation all the quantum fluctuation is a time-translation invariant, see for instance the Hamilton-Jacobi Eq. (4.41); therefore it may be further resumed as the *fluctuation factor*:

$$F\left(t_b - t_a\right) \equiv \int_{\delta x(t_a)=0}^{\delta x(t_b)=0} \mathcal{D}\delta x(t) \exp\left\{\frac{i}{\hbar}\int_{t_a}^{t_b}\left[\begin{array}{l}\alpha(t)\delta x + \beta(t) y\delta\dot{x} \\ +\gamma(t)\delta\dot{x}^2\end{array}\right]dt\right\} \tag{4.77}$$

- Looking at the terms appearing in the whole Lagrangian (4.72) and to those present on the factor (4.77) it seems that once the factor (4.77) is known for a given Lagrangian, say L, then the same is characterizing also the modified one with the terms that are not present in the forms (4.77):

$$\tilde{L} = L + \lambda(t)x + \chi(t)\dot{x} + \sigma(t) \tag{4.78}$$

- The resulting working path integral of the propagator now simply reading as:

$$\left(x_b, t_b; x_a, t_a\right) = F\left(t_b - t_a\right)\exp\left\{\frac{i}{\hbar}S_{cl}[x_{cl}, \dot{x}_{cl}, t]\right\} \tag{4.79}$$

gives intuitive inside of what path integral formalism of quantum mechanics really does: corrects the classical paths by the *quantum fluctuations viewed as amplitude of the (semi) classical wave*.

Next, the big challenge is to compute the above fluctuation factor (4.79); here there are two possibilities of approach. One is considering the fluctuations as a Fourier series expansion so that directly (although through enough involving procedure) solving the multiple integrals appearing in Eq. (4.77). Yet, this route was that originally proposed by Feynman in his quantum mechanically devoted monograph (Feynman & Hibbs, 1965), while recently refined in an extended textbook (Kleinert, 2004).

The second way is trickier, although with its limitation, but avoids performing the direct integration prescribed by Eq. (4.77), while instructive since computing the quantum fluctuation again in terms of classical path action (Dittrich & Reuter, 1994), however through employing the present first two propagator properties, the group property (4.65) and the delta-Dirac limit (4.67), to the quantum wave (4.79).

As such, combining the stipulated propagator properties, one starts equivalently writing

$$\begin{aligned}\delta\left(x_b - x_a\right) &= \left(x_b, t; x_a, t\right) \\ &= \int \left(x_b, t; x, 0\right)\left(x, 0; x_a, t\right) dx = \int \left(x_b, t; x, 0\right)\left(x_a, t; x, 0\right)^* dx \end{aligned} \quad (4.80)$$

where the last identity follows by employing the identity between the retarded (+) and advanced (–) Green functions (Greiner & Reinhardt, 1994)

$$G^+\left(x_b, t_b; x_a, t_a\right) = \left[G^-\left(x_a, t_a; x_b, t_b\right)\right]^* \quad (4.81)$$

combined with the propagator-Green function relationship (4.45), here supplemented with the advanced propagator version:

$$\left(x_a, t_a; x_b, t_b\right) = -iG^-\left(x_a, t_a; x_b, t_b\right) \quad (4.82)$$

Now, the propagators from Eq. (4.80) may be written immediately from the general form (4.79):

$$\left(x_b, t; x, 0\right) = F\left(t\right)\exp\left\{\frac{i}{\hbar} S_{cl}\left(x_b, t; x, 0\right)\right\} \quad (4.83)$$

$$\left(x_a, t; x, 0\right)^* = F^*\left(t\right)\exp\left\{-\frac{i}{\hbar} S_{cl}\left(x_a, t; x, 0\right)\right\} \quad (4.84)$$

which help in rewrite (4.80) as:

$$\delta\left(x_b - x_a\right) = \int dx \left|F(t)\right|^2 \exp\left\{\frac{i}{\hbar}\left[S_{cl}\left(x_b, t; x, 0\right) - S_{cl}\left(x_a, t; x, 0\right)\right]\right\}$$

$$\underset{\Delta x = x_b - x_a}{\overset{x_b = x_a + \Delta x}{=}} \left|F(t)\right|^2 \int dx \exp\left\{\frac{i}{\hbar}\begin{bmatrix} S_{cl}\left(x_a + \Delta x, t; x, 0\right) \\ -S_{cl}\left(x_a, t; x, 0\right) \end{bmatrix}\right\}$$

$$= \left|F(t)\right|^2 \int dx \exp\left\{\frac{i}{\hbar}\frac{\partial S_{cl}\left(x_a, t; x, 0\right)}{\partial x_a}\Delta x\right\}$$

$$= \left|F(t)\right|^2 \int dx \exp\left\{\frac{i}{\hbar}\frac{\partial S_{cl}\left(x_a, t; x, 0\right)}{\partial x_a}\left(x_b - x_a\right)\right\} \tag{4.85}$$

Next, assuming the notation:

$$s(x) \equiv \frac{\partial S_{cl}\left(x_a, t; x, 0\right)}{\partial x_a} \tag{4.86}$$

if its derivative $ds(x)/dx$ is independent of x it goes out the integral if the changing in variable may apply on Eq. (4.85) leaving with the identity:

$$\delta\left(x_b - x_a\right) = \frac{2\pi\hbar\left|F(t)\right|^2}{\left|ds/dx\right|} \underbrace{\int \frac{ds}{2\pi\hbar} \exp\left\{\frac{i}{\hbar}\left(x_b - x_a\right)s\right\}}_{\delta\left(x_b - x_a\right)} \tag{4.87}$$

from where the quantum fluctuation factor follows at once with the analytical general form:

$$F(t) = \sqrt{\frac{1}{2\pi\hbar}\left|\frac{ds}{dx}\right|} \underset{eq.(4.86)}{=} \frac{1}{\sqrt{2\pi\hbar}}\left|\frac{\partial^2 S_{cl}\left(x_a, t; x, 0\right)}{\partial x \partial x_a}\right|^{1/2} \tag{4.88}$$

With expression (4.88) the propagator (4.79) is fully expressed in terms of classical action as:

$$\left(x_b, t_b; x_a, t_a\right) = \frac{1}{\sqrt{2\pi\hbar}}\left|\frac{\partial^2 S_{cl}\left(x_a, t; x, 0\right)}{\partial x \partial x_a}\right|^{1/2} \exp\left\{\frac{i}{\hbar}S_{cl}\left(x_b, t_b; x_a, t_a\right)\right\},\ t = t_b - t_a \tag{4.89}$$

or in the more appealing form:

$$\left(x_b,t_b;x_a,t_a\right)=\frac{1}{\sqrt{2\pi\hbar}}\left|\frac{\partial^2 S_{cl}\left(x_b,t_b;x_a,t_a\right)}{\partial x_b\partial x_a}\right|^{1/2}\exp\left\{\frac{i}{\hbar}S_{cl}\left(x_b,t_b;x_a,t_a\right)\right\} \quad (4.90)$$

usually referred to as the Van Vleck-Pauli-Morette formula, emphasizing on the importance of solving the classical problem for a given canonical Lagrangian (Laidlaw & DeWitt-Morette, 1971; Peak & Inomata, 1969).

However, the path integral solution (4.90) has to be used with two amendments:

- the procedure is valid only when the quantity (4.86), here rewritten in the spirit of Eq. (4.90) as $\partial S_{cl}\left(x_b,t_b;x_a,t_a\right)/\partial x_a$, performed respecting one end-point coordinate remains linear in the other space (end-point) coordinate x_b, so that the identity (4.87) holds; this is true for the quadratic Lagrangian's of type (4.72) but not when higher orders are involved, when the previously stipulated Fourier analysis has to be undertaken (one such case will be in foregoing sections presented).
- In the case the formula (4.90) is applicable, i.e., when previous condition applies, the obtained result has to be still verified to recover the delta-Dirac function in the limit:

$$\lim_{t_b\to t_a}\left(x_b,t_b;x_a,t_a\right)=\delta\left(x_b-x_a\right) \quad (4.91)$$

in accordance with the implemented recipe, see Eq. (4.80); usually this step is providing additional phase correction to the solution (4.90).

The present algorithm is in next exemplified on two paradigmatic quantum problems: the free motion and the motion under harmonic oscillator influence. In each case the set of the classical action will almost solve the entire path integral problem.

4.3.2 PATH INTEGRAL FOR THE FREE PARTICLE

Given a free particle with the Lagrangian

$$L_{(0)}\left(x,\dot{x},t\right)=\frac{m}{2}\dot{x}^2 \quad (4.92)$$

it leaves by means of Euler-Lagrange equation

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right)=\frac{\partial L}{\partial x} \tag{4.93}$$

to the classical (Newtonian) motion:

$$\ddot{x}_{cl}(t)=0 \tag{4.94}$$

with the obvious solution

$$x_{cl}(t)=x_a+\frac{x_b-x_a}{t_b-t_a}\left(t-t_a\right) \tag{4.95}$$

fulfilling the boundary conditions:

$$x_{cl}(t_a)=x_a;\, x_{cl}(t_b)=x_b \tag{4.96}$$

being these endpoints the states where the system is observable, i.e., when quantum fluctuations vanishes, see Eq. (4.71) and Figure 4.2.

Replacing solution (4.95) back in Lagrangian (4.92) the classical action is immediately found:

$$S_{(0)cl}\left(x_b,t_b;x_a,t_a\right)=\int_{t_a}^{t_b}L_{(0)}\left(x_{cl},\dot{x}_{cl},t\right)dt=\frac{m}{2}\int_{t_a}^{t_b}\dot{x}_{cl}^2(t)dt=\frac{m}{2}\frac{\left(x_b-x_a\right)^2}{t_b-t_a} \tag{4.97}$$

Next, the quantity (4.86) is firstly evaluated in the spirit of Eq. (4.90) as

$$s_{(0)}(x)=\frac{\partial S_{(0)cl}\left(x_b,t_b;x_a,t_a\right)}{\partial x_a}=\frac{m}{t_b-t_a}\left(x_b-x_a\right) \tag{4.98}$$

and recognized as linear in the other end-point space coordinate x_b. Thus, the formula (4.90) may be applied, with the actual yield:

$$\left(x_b,t_b;x_a,t_a\right)_{(0)}=\sqrt{\frac{m}{2\pi\hbar\left(t_b-t_a\right)}}\exp\left\{\frac{i}{\hbar}\frac{m}{2}\frac{\left(x_b-x_a\right)^2}{t_b-t_a}\right\} \tag{4.99}$$

Finally, the result of Eq. (4.99) has to be arranged so that to satisfy the limit (4.91) as well. For that we use the delta-Dirac representation:

$$\delta\left(x_b - x_a\right) = \frac{1}{\sqrt{\pi}} \lim_{T\to 0}\left\{\frac{1}{\sqrt{T}} \exp\left[-\frac{\left(x_b - x_a\right)^2}{T}\right]\right\} \tag{4.100}$$

Comparison between Eqs. (4.99) and (4.100) leads with identification:

$$\frac{1}{T} = -\frac{im}{2\hbar\left(t_b - t_a\right)} = \frac{m}{2i\hbar\left(t_b - t_a\right)} \tag{4.101}$$

thus correcting the factor of Eq. (4.99) so that to have the correct limiting path integral solution:

$$\left(x_b, t_b; x_a, t_a\right)_{(0)} = \sqrt{\frac{m}{2\pi i\hbar\left(t_b - t_a\right)}} \exp\left\{\frac{i}{\hbar}\frac{m}{2}\frac{\left(x_b - x_a\right)^2}{t_b - t_a}\right\} \tag{4.102}$$

Remarkably, this solution is indeed identical with the Green function of the free particle, until the complex factor of Eq. (4.45), this way confirming the reliability of the path integral approach. Moreover, beside of its foreground character in quantum mechanics, the present path integral of the free particle can be further used in the paradigmatic vibrational motion by using the basic rules in using path integrals propagator for density computations:

- The reliable application of the density computation upon the partition function algorithm, see Eqs. (4.43) and (4.44), prescribes the transformation of the obtained quantum result in the quantum statistical counterpart by means of Wick transformation (4.33) supplemented by the trigonometric to hyperbolic functions conversions;
- In computation of the path integral propagator the workable *Van Vleck-Pauli-Morette formula* looks like

$$\left(x_b, t_b; x_a, t_a\right) = \sqrt{\frac{1}{2\pi i\hbar}\left|\frac{\partial^2 S_{cl}\left(x_b, t_b; x_a, t_a\right)}{\partial x_b \partial x_a}\right|} \exp\left\{\frac{i}{\hbar} S_{cl}\left(x_b, t_b; x_a, t_a\right)\right\} \tag{4.103}$$

with the complex factor "i" included, as confirmed by both the free and harmonic oscillator quantum motions, for being used for classical actions linear upon derivation respecting one of the end-point space coordinates in the other one; yet the formula (4.103) should be always checked for fulfilling the limiting (4.91) delta-Dirac function for simultaneous events for any applied potential.

Beside of these working rules, regaining the energy quantification of free electrons in solid state (motion within the infinite high box) as well as the obligatory Bohr quantification for the continuous deformation of the path on the circle (Kleinert, 2004; Dittrich & Reuter, 1994), will complete the 3-fold fundamental types of quantum evolution (i.e., covering the rotation, vibration and translations for motion in atomic quantified circles, in molecule and along the solid state bands, respectively) as loaded and reloaded from various perspectives through this volume, see the preceding chapters.

4.3.3 PATH INTEGRAL FOR MOTION AS THE HARMONIC OSCILLATOR

The characteristic Lagrangian of the harmonic oscillator,

$$L_{(\omega)}\left(x,\dot{x},t\right)=\frac{m}{2}\dot{x}^2-\frac{m}{2}\omega^2x^2 \tag{4.104}$$

provides, when considered in the Euler-Lagrange equation (4.93), the classical equation of motion:

$$\ddot{x}_{cl}(t)+\omega^2x_{cl}(t)=0 \tag{4.105}$$

with the well known solution

$$x_{cl}(t)=C\sin\left(\omega t+\varphi\right) \tag{4.106}$$

specialized on the end-point events of motion as:

$$x_a=x_{cl}(t_a)=C\sin\left(\omega t_a+\varphi\right) \tag{4.107}$$

$$x_b = x_{cl}(t_b) = C\sin\left(\omega t_b + \varphi\right) \tag{4.108}$$

In the same way as done for free motion, see solution (4.95), worth rewritten the actual classical solution (4.106) in terms of relations (4.107) and (4.108), for instance as

$$\begin{aligned} x_{cl}(t) &= C\sin\left[\omega\left(t-t_a\right)+\left(\omega t_a+\varphi\right)\right] \\ &= \underbrace{C\cos\left(\omega t_a+\varphi\right)}_{\dot{x}_a/\omega}\sin\left[\omega\left(t-t_a\right)\right] \\ &\quad + \underbrace{C\sin\left(\omega t_a+\varphi\right)}_{x_a}\cos\left[\omega\left(t-t_a\right)\right]; \\ x_{cl}(t) &= \frac{1}{\omega}\dot{x}_a\sin\left[\omega\left(t-t_a\right)\right]+x_a\cos\left[\omega\left(t-t_a\right)\right] \end{aligned} \tag{4.109}$$

or similarly as:

$$x_{cl}(t) = \frac{1}{\omega}\dot{x}_b\sin\left[\omega\left(t-t_b\right)\right]+x_b\cos\left[\omega\left(t-t_b\right)\right] \tag{4.110}$$

On the other side the classical action of the Lagrangian (4.104) looks like:

$$\begin{aligned} S_{(\omega)cl}\left(x_b,t_b;x_a,t_a\right) &= \int_{t_a}^{t_b} L_{(\omega)}\left(x_{cl},\dot{x}_{cl},t\right)dt \\ &= \frac{m}{2}\int_{t_a}^{t_b}\left[\left(\frac{dx_{cl}}{dt}\right)\left(\frac{dx_{cl}}{dt}\right)-\omega^2 x_{cl}^2\right]dt \\ &= \frac{m}{2}\int_{t_a}^{t_b}\left[\frac{d}{dt}\left(x_{cl}\dot{x}_{cl}\right)-x_{cl}\ddot{x}_{cl}-\omega^2 x_{cl}^2\right]dt \\ &= \left[\frac{m}{2}x_{cl}(t)\dot{x}_{cl}(t)\right]_{t_a}^{t_b}-\frac{m}{2}\int_{t_a}^{t_b}\underbrace{\left(\ddot{x}_{cl}+\omega^2 x_{cl}\right)}_{=0}x_{cl}dt \\ &\qquad\qquad eq.\,(4.105) \\ &= \frac{m}{2}\left[x_b(t_b)\dot{x}_b(t_b)-x_a(t_a)\dot{x}_a(t_a)\right] \end{aligned} \tag{4.111}$$

Now, in order having classical action in terms of only space-time coordinate of the ending points, one has to replace the end-point velocities in Eq. (4.111) with the aid of relations (4.109) and (4.110) in which the current time is taken as the $t = t_b$ and $t = t_a$, respectively; thus we firstly get:

$$\dot{x}_a = \frac{\omega}{\sin\left[\omega\left(t_b - t_a\right)\right]}\left\{x_b - x_a \cos\left[\omega\left(t_b - t_a\right)\right]\right\} \tag{4.112}$$

$$\dot{x}_b = \frac{\omega}{\sin\left[\omega\left(t_b - t_a\right)\right]}\left\{-x_a + x_b \cos\left[\omega\left(t_b - t_a\right)\right]\right\} \tag{4.113}$$

then we form the needed products:

$$x_b \dot{x}_b = \frac{\omega}{\sin\left[\omega\left(t_b - t_a\right)\right]}\left\{x_b^2 \cos\left[\omega\left(t_b - t_a\right)\right] - x_a x_b\right\} \tag{4.114}$$

$$x_a \dot{x}_a = \frac{\omega}{\sin\left[\omega\left(t_b - t_a\right)\right]}\left\{-x_a^2 \cos\left[\omega\left(t_b - t_a\right)\right] + x_a x_b\right\} \tag{4.115}$$

to finally replace them in expression (4.111) to provide the computed classical action:

$$S_{(\omega)cl}\left(x_b, t_b; x_a, t_a\right) = \frac{m\omega}{2\sin\left[\omega\left(t_b - t_a\right)\right]}\left\{\begin{matrix}\left(x_a^2 + x_b^2\right) \\ \cos\left[\omega\left(t_b - t_a\right)\right] - 2x_a x_b\end{matrix}\right\} \tag{4.116}$$

Note that the correctness of Eq. (4.116) may be also checked by imposing the limit $\omega \to 0$ in which case the previous free motion has to be recovered; indeed by employing the consecrated limit

$$\lim_{y \to 0} \frac{\sin y}{y} = 1 \tag{4.117}$$

one immediately get:

$$\lim_{\omega \to 0} S_{(\omega)cl}\left(x_b, t_b; x_a, t_a\right)$$

$$= \frac{m}{2(t_b - t_a)} \underbrace{\lim_{\omega \to 0} \frac{\omega(t_b - t_a)}{\sin\left[\omega(t_b - t_a)\right]}}_{=1} \underbrace{\lim_{\omega \to 0} \left\{ \begin{matrix} \left(x_a^2 + x_b^2\right)\cos\left[\omega(t_b - t_a)\right] \\ -2x_a x_b \end{matrix} \right\}}_{(x_b - x_a)^2}$$

$$= \frac{m}{2} \frac{(x_b - x_a)^2}{t_b - t_a}$$

$$= S_{(0)cl}(x_b, t_b; x_a, t_a) \tag{4.118}$$

Such kind of check is most useful and has to hold also for the quantum propagator as a whole. Going to determine it one has to reconsider the classical action (4.116) so that the quantity (4.86) is directly evaluated in the spirit of Eq. (4.90) as:

$$\frac{\partial S_{(\omega)cl}(x_b, t_b; x_a, t_a)}{\partial x_a} = \frac{m\omega}{\sin\left[\omega(t_b - t_a)\right]} \left\{ x_a \cos\left[\omega(t_b - t_a)\right] - x_b \right\} \tag{4.119}$$

thus again encountering it as being linear in the other end-point coordinate x_b, being this the fortunate situation in which the previous section algorithm for path integral computation may be applied though the expression (4.90), here manifested with the harmonic oscillator result:

$$(x_b, t_b; x_a, t_a) = \sqrt{\frac{m\omega}{2\pi\hbar \sin\left[\omega(t_b - t_a)\right]}} \exp\left\{ \frac{i}{\hbar} \frac{m\omega}{2\sin\left[\omega(t_b - t_a)\right]} \left\{ \begin{matrix} \left(x_a^2 + x_b^2\right) \\ \cos\left[\omega(t_b - t_a)\right] - 2x_a x_b \end{matrix} \right\} \right\} \tag{4.120}$$

Yet, as above was the case for the classical action itself, also the pre-exponential quantum fluctuation factor of Eq. (4.120) has to overlap with that appearing in the path integral of free motion of Eq. (4.102) under the limit $\omega \to 0$:

$$\lim_{\omega \to 0} \sqrt{\frac{m\omega}{2\pi\hbar \sin\left[\omega(t_b - t_a)\right]}} \underset{eq.(4.117)}{=} \sqrt{\frac{m}{2\pi\hbar(t_b - t_a)}} \tag{4.121}$$

Thus we have to have the propagator (4.120) with the exponential pre-factor gaining an appropriate placed complex factor "i:

$$\left(x_b,t_b;x_a,t_a\right)_{(\omega)}=\sqrt{\frac{m\omega}{2\pi i\hbar\sin\left[\omega\left(t_b-t_a\right)\right]}}\quad\exp\left\{\begin{array}{l}\dfrac{i}{\hbar}\dfrac{m\omega}{2\sin\left[\omega\left(t_b-t_a\right)\right]}\\ \times\left\{\left(x_a^2+x_b^2\right)\cos\left[\omega\left(t_b-t_a\right)\right]-2x_ax_b\right\}\end{array}\right\} \tag{4.122}$$

This is the searched propagator of the (electronic) motion under the harmonic oscillating potential, computed by means of path integral; it provides the canonical density to be implemented in the DFT algorithm (4.43) and (4.44):

$$\rho_{\otimes}\left(x,t_b-t_a\right)=\left(x,t_b;x,t_a\right)_{(\omega)}=\sqrt{\frac{m\omega}{2\pi i\hbar\sin\left[\omega\left(t_b-t_a\right)\right]}}\times\exp\left\{\frac{i}{\hbar}\frac{m\omega\left(\cos\left[\omega\left(t_b-t_a\right)\right]-1\right)}{\sin\left[\omega\left(t_b-t_a\right)\right]}x^2\right\} \tag{4.123}$$

Yet, for practical implementations, the passage from quantum mechanics (QM) to quantum statistics (QS) is to be considered based on the Wick transformation (4.33) here rewritten as:

$$\left(t_b-t_a\right)\rightarrow-i\hbar\beta\equiv-i\left(\tau_b-\tau_a\right) \tag{4.124}$$

providing the Euler based trigonometric to hyperbolic function conversions (by analytic continuations):

$$\begin{aligned}\sin\omega\left(t_b-t_a\right)&=\frac{1}{i}\frac{e^{i\omega\left(t_b-t_a\right)}-e^{-i\omega\left(t_b-t_a\right)}}{2}\rightarrow\frac{1}{i}\frac{e^{\omega\left(\tau_b-\tau_a\right)}-e^{-i\omega\left(\tau_b-\tau_a\right)}}{2}\\&=\frac{1}{i}\sinh\omega\left(\tau_b-\tau_a\right)\end{aligned} \tag{4.125}$$

$$\cos\omega\left(t_b-t_a\right)=\frac{e^{i\omega\left(t_b-t_a\right)}+e^{-i\omega\left(t_b-t_a\right)}}{2}\rightarrow\frac{e^{\omega\left(\tau_b-\tau_a\right)}+e^{-i\omega\left(\tau_b-\tau_a\right)}}{2}$$
$$=\cosh\omega\left(\tau_b-\tau_a\right) \tag{4.126}$$

allowing for density (4.123) the counterpart formulation:

$$\rho_{\otimes}\left(x,\tau_b-\tau_a\right)=\sqrt{\frac{m\omega}{2\pi\hbar\sinh\left[\omega\left(\tau_b-\tau_a\right)\right]}}$$
$$\exp\left\{-\frac{1}{\hbar}\frac{m\omega\left(\cosh\left[\omega\left(\tau_b-\tau_a\right)\right]-1\right)}{\sinh\left[\omega\left(\tau_b-\tau_a\right)\right]}x^2\right\} \tag{4.127}$$

The uni-particle (electronic) density (4.127) is then used for computing the harmonic oscillator partition function:

$$Z_{\omega}=\int_{-\infty}^{+\infty}\rho_{\otimes}\left(x,\tau_b-\tau_a\right)dx$$
$$=\sqrt{\frac{m\omega}{2\pi\hbar\sinh\left[\omega\left(\tau_b-\tau_a\right)\right]}}$$
$$\int_{-\infty}^{+\infty}\exp\left\{-\frac{1}{\hbar}\frac{m\omega\left(\cosh\left[\omega\left(\tau_b-\tau_a\right)\right]-1\right)}{\sinh\left[\omega\left(\tau_b-\tau_a\right)\right]}x^2\right\}dx$$
$$=\sqrt{\frac{m\omega}{2\pi\hbar\sinh\left[\omega\left(\tau_b-\tau_a\right)\right]}}\sqrt{\frac{\pi\hbar\sinh\left[\omega\left(\tau_b-\tau_a\right)\right]}{m\omega\left(\cosh\left[\omega\left(\tau_b-\tau_a\right)\right]-1\right)}}$$
$$=\sqrt{\frac{1}{2\left(\cosh\left[\omega\left(\tau_b-\tau_a\right)\right]-1\right)}} \tag{4.128}$$

Now using the "double angle" formula:

$$\cosh 2y=\cosh^2 y+\sinh^2 y=2\cosh^2 y-1=2\sinh^2 y+1 \tag{4.129}$$

partition function (4.128) further becomes:

$$Z_{\omega} = \frac{1}{2\sinh\left[\dfrac{\omega(\tau_b - \tau_a)}{2}\right]} \overset{eq.(4.124)}{=} \frac{1}{2\sinh\left[\dfrac{\omega\hbar\beta}{2}\right]} \tag{4.130}$$

Remarkably, the result (4.130) recovers also the energy quantification of the quantum motion under the harmonic oscillator influence, through the successive transformations:

$$\begin{aligned} Z_{\omega} &= \frac{1}{\exp(\omega\hbar\beta/2) - \exp(-\omega\hbar\beta/2)} \\ &= \exp(-\omega\hbar\beta/2)\frac{1}{1-\exp(-\omega\hbar\beta)} \\ &= \exp(-\omega\hbar\beta/2)\sum_{n=0}^{\infty}\left[\exp(-\omega\hbar\beta)\right]^n \\ &= \exp(-\omega\hbar\beta/2)\sum_{n=0}^{\infty}\left[\exp(-n\omega\hbar\beta)\right] \\ &= \sum_{n=0}^{\infty}\exp\left[-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right] \end{aligned} \tag{4.131}$$

Comparing the expression (4.131) with the canonical formulation of the partition function

$$Z \equiv \sum_{n=0}^{\infty}\exp\left[-\beta E_n\right] \tag{4.132}$$

there follows immediately the harmonic oscillator energy quantification:

$$E_n(\omega) = \hbar\omega\left(n+\frac{1}{2}\right) \tag{4.133}$$

in perfect agreement with the consecrated expression, see Eqs. (2.525), (3.149), (3.231), and (3.280).

4.3.4 PATH INTEGRAL REPRESENTATION FOR THE BOHR'S ATOM

Consider a particle in a circular closed path motion (i.e., an orbit continuously deformed into a circle), with the specific parameters:

- the fixed (not necessarily observed) end-points $\varphi = 0$ & $\varphi = 2\pi$;
- the circular length parameter $s_{a...b}$ along the circle length L.

This circular motion, being along a simple connected line (the circle) can be projected on the free-particle (line) motion (on real space $\mathfrak{R}$) over which specific constraints are imposed to regain the circular path and motion towards the present path integral model of the Bohr's atom. Therefore, one re-considers the free-motion propagator of Eq. (4.102)

$$\left(x_b^{(n)}, t_b; x_a, t_a\right)_{(0,\mathfrak{R})} = \sqrt{\frac{m}{2\pi i\hbar\left(t_b - t_a\right)}} \exp\left\{\frac{i}{\hbar}\frac{m}{2}\frac{\left(x_b^{(n)} - x_a\right)^2}{t_b - t_a}\right\} \quad (4.134)$$

by assuming that while going from x_a to $x_b^{(n)}$ the particle covered the entire circular orbit as much as n-times the so that adding nL to the initial circular parameter on ring, that writes:

$$\begin{cases} x_b^{(n)} - x_a = s_b - s_a + nL \equiv \Delta s + nL \\ t_b - t_a \equiv \Delta t \end{cases} \quad (4.135)$$

Such that the evolution amplitude (the propagator) (4.134) acquires the atomic circular orbit information under the working form

$$\left(s_b, t_b; s_a, t_a\right)_L = \sqrt{\frac{m}{2\pi i\hbar\Delta t}} \exp\left\{\frac{i}{\hbar}\frac{m}{2}\frac{\left(\Delta s + nL\right)^2}{\Delta t}\right\} \quad (4.136)$$

At this point one would seek to unfold this information in a sum of orbit paths in order to correctly describe the particle motion within atomic circular orbits; to this aim, one would benefit from turning back the exponential form of Eq. (4.136) into a path integral; this can be achieved in two steps:

- Firstly, the Poisson formula (4.26) is employed to provide the extended useful integral formulation

$$\int_{-\infty}^{+\infty} e^{-\left(ay^2+2by+c\right)}dy = e^{\frac{b^2-ac}{a}}\int_{-\infty}^{+\infty} e^{-\frac{(ay+b)^2}{a}}dy = \frac{1}{\sqrt{a}}e^{\frac{b^2-ac}{a}}\int_{-\infty}^{+\infty} e^{-x^2}dx = \sqrt{\frac{\pi}{a}}e^{\frac{b^2-ac}{a}} \quad (4.137)$$

which is adapted for the present purpose ($c = 0$) to the identity

$$\frac{1}{\sqrt{a\pi}}e^{\frac{b^2}{a}} = \frac{1}{\pi}\int_{-\infty}^{+\infty} e^{-\left(ap^2+2bp\right)}dp \quad (4.138)$$

of which l.h.s. may be recognized in Eq. (4.136) rearranged as

$$\left(s_b,t_b;s_a,t_a\right)_L = \sqrt{\frac{m}{8\hbar}}\frac{1}{\sqrt{\pi}}\sqrt{\frac{4}{i\Delta t}}\exp\left\{\frac{4}{i\Delta t}\left[\frac{1}{2i}\sqrt{\frac{m}{2\hbar}}\left(\Delta s+nL\right)\right]^2\right\} \quad (4.139)$$

This way the circular propagator may be considered as the path integral

$$G\left(\Delta s,\Delta t\right)_L = \frac{1}{\pi}\sqrt{\frac{m}{8\hbar}}\int\exp\left\{-i\frac{\Delta t}{4}p^2+ip\sqrt{\frac{m}{2\hbar}}\left(\Delta s+nL\right)\right\}dp \quad (4.140)$$

Which can be further rewritten by changing the integrand in order to achieve the non-dimensional quantities under exponential, by the transformation

$$p \to p\sqrt{\frac{2}{m\hbar}} \quad (4.141)$$

leading with the working propagator

$$G\left(\Delta s,\Delta t\right)_L = \frac{1}{2\pi\hbar}\int\exp\left\{-i\frac{\Delta t}{2m\hbar}p^2+\frac{i}{\hbar}p\left(\Delta s+nL\right)\right\}dp \quad (4.142)$$

- The second step is considering in Eq. (4.142) of the complete orbits as factorization contribution

$$G(\Delta s,\Delta t)_L = \frac{1}{2\pi\hbar}\int\left[e^{\frac{i}{\hbar}pnL}\right]e^{-i\frac{\Delta t}{2m\hbar}p^2+\frac{i}{\hbar}p\Delta s}dp \tag{4.143}$$

And to consider on this last expression all possible paths (n-th order) by which the final circular position on orbit is reached; equivalently, this means summing up over all such possibilities (like in counting states within the partition functions) to yield

$$G(\Delta s,\Delta t)_L = \frac{1}{2\pi\hbar}\int\left[\sum_{n=-\infty}^{+\infty}e^{\frac{i}{\hbar}pnL}\right]e^{-i\frac{\Delta t}{2m\hbar}p^2+\frac{i}{\hbar}p\Delta s}dp \tag{4.144}$$

Now we are in position to recognize the Poisson summation (the comb) formula (see Appendix A.1.2) linking the exponential fluctuations with the delta Dirac point-contributions

$$\sum_{n=-\infty}^{+\infty}e^{i2\pi nx} = \sum_{n=-\infty}^{+\infty}\delta(x-n) \tag{4.145}$$

Specifically, in the case of Eq. (4.144), one has in the first instance the transformation

$$\sum_{n=-\infty}^{+\infty}e^{\frac{i}{\hbar}pnL} = \sum_{n=-\infty}^{+\infty}e^{i2\pi n\frac{pL}{2\pi\hbar}} = \sum_{n=-\infty}^{+\infty}\delta\left(\frac{pL}{2\pi\hbar}-n\right) = \frac{2\pi\hbar}{L}\sum_{n=-\infty}^{+\infty}\delta\left(p-\frac{2\pi\hbar}{L}n\right) \tag{4.146}$$

where the Dirac factorization property was considered

$$\delta\left[a(X-Y)\right] = \frac{1}{|a|}\delta(X-Y) \tag{4.147}$$

One has therefore the actual propagator of the Bohr's atom

$$G(\Delta s,\Delta t)_L = \frac{1}{L}\int\sum_{n=-\infty}^{+\infty}\delta\left(p-\frac{2\pi\hbar}{L}n\right)e^{-i\frac{\Delta t}{2m\hbar}p^2+\frac{i}{\hbar}p\Delta s}dp \tag{4.148}$$

Which allows further solution my means of the filtration property of delta-Dirac function, see Eq. (2.11), to get the almost final result, namely:

$$G\left(\Delta s,\Delta t\right)_L=\frac{1}{L}\sum_{n=-\infty}^{+\infty}\exp\left\{-i\frac{\Delta t}{2m\hbar}\left(\frac{2\pi\hbar}{L}n\right)^2+i2\pi n\frac{\Delta s}{L}\right\} \tag{4.149}$$

The final results will be displayed in terms of the natural parameter for the circular motion, i.e., by the angle φ: for a radius R of the given orbit, one readily can complete the list of Eq. (4.135) with the actual one including the inertia momentum (I):

$$\begin{cases} L=2\pi R \\ \Delta s=R\left(\varphi_b^{(n)}-\varphi_a\right)\overset{!}{=}R\varphi \\ p=mR\dot{\varphi} \\ t_b-t_a\equiv\Delta t \\ I=mR^2 \end{cases} \tag{4.150}$$

Now we arrive to the quantification conclusions:

- The delta Dirac function in Eq. (4.146) gives the momentum quantification

$$p=\frac{2\pi\hbar}{L}n \tag{4.151}$$

Which is quite equivalent with the phenomenological deduction in Eq. (1.79) when considering also length-radius connection from (4.150); moreover, with the present approach also the kinetic momentum is found quantified since:

$$n\hbar=\frac{pL}{2\pi}=\frac{\left(mR\dot{\varphi}\right)\left(2\pi R\right)}{2\pi}=mR^2\dot{\varphi}=L_z \tag{4.152}$$

thus completing the Bohr's quantification with the so-called "first integral" of motion, characteristic to the orbital motion itself, apart of the de Broglie closure quantification on (whatever) orbit (4.151).

Nevertheless, the total energy on orbit is directly quantified by the kinetic energy information absorbing all potential information (by circular motion and closing paths), i.e., directly writing as:

$$E_n = \frac{p^2}{2m} = \frac{\hbar^2}{2mR^2} n^2 = \frac{\hbar^2}{2I} n^2 \tag{4.153}$$

certainly in accordance with the phenomenological expression obtained from optimum quantities in Eq. (1.82), apart of the minus sign (indicating the binding energy nature).

Eventually, the atomic Bohr's propagator (4.149) finally looks like

$$G(R\varphi, \Delta t) = \frac{1}{2\pi R} \sum_{n=-\infty}^{+\infty} \exp\left\{ -i \frac{\Delta t}{2I} \hbar n^2 + in\varphi \right\} \tag{4.154}$$

Or under the non-dimensional form:

$$G(\varphi, \Delta t) = RG(R\varphi, \Delta t) = \frac{1}{2\pi} \sum_{n=-\infty}^{+\infty} \exp\left\{ -i \frac{\Delta t}{2I} \hbar n^2 + in\varphi \right\} \tag{4.155}$$

such that the evolution amplitude of the propagator is shaped as a trigonometric normalized output itself. Worth noting that accommodating the Bohr's atom and quantification within path integral formalism gives it strength and elegancy, while offering enough consistency and richness in quantum information in order to have preeminence in treating complex quantum structure and interactions.

4.3.5 PATH INTEGRAL FOR MOTION IN THE QUANTUM WELL

The particle in a quantum well of potential

$$V(x) = \begin{cases} 0 & \ldots \ 0 < x < L \\ \infty & \ldots \ x \le 0 \ \& \ x \ge L \end{cases} \tag{4.156}$$

may be described as a combination between:

- the free particle propagation due to the translational movement inside the walls
- the Bohr's atom movement due to the closing paths by bouncing off the walls

However, there are also two characteristics, due to the collisions and the turning points along the path on the walls, namely:

- starting the initial point (x_a, t_a) the final point may be reached either from the direct path (x_b, t_b) as well as from the opposite direction of path $(-x_b, t_b)$; therefore, the propagator of the particle inside the quantum well should be regarded as a superposition of two free particle contributions

$$(x_b, t_b; x_a, t_a)_{well} = \sqrt{\frac{m}{2\pi i\hbar(t_b - t_a)}} \left\{ \begin{array}{l} \exp\left[\frac{i}{\hbar} \frac{m}{2} \frac{(x_b - x_a)^2}{t_b - t_a} \right] \\ -\exp\left[\frac{i}{\hbar} \frac{m}{2} \frac{(x_b - x_a)^2}{t_b - t_a} \right] \end{array} \right\} \tag{4.157}$$

- consequently the space-time information in Eq. (4.135) is now modified such that, due to the wall turning points, the traveled space is *doubled* by the forward and backward movements such that the for the *r*-th trip between walls we will have

$$\begin{cases} x_b - x_a = x_f - x_i + 2rL \\ t_b - t_a \equiv \Delta t \end{cases} \tag{4.158}$$

Combining these information, as previously for the Bohr's atom, with the sum over infinite histories with the same scenario and output, while performing for each of the exponentials of Eq. (4.157) the same analytical transformation by means of Eq. (4.138) as previously done for atomic circular motion, we adapt the result (4.142) to the present quantum well situation to firstly get

$$G\left(x_f;x_i,\Delta t\right)_L=\frac{1}{2\pi\hbar}\sum_{r=-\infty}^{\infty}\int\left[\begin{array}{l}\exp\left\{-i\dfrac{\Delta t}{2m\hbar}p^2+\dfrac{i}{\hbar}p\left(x_f-x_i+2rL\right)\right\}\\-\exp\left\{-i\dfrac{\Delta t}{2m\hbar}p^2+\dfrac{i}{\hbar}p\left(-x_f-x_i+2rL\right)\right\}\end{array}\right]dp \tag{4.159}$$

from where one may separate the final point contribution and apply the sum contribution over paths on the specific changing phase (by $2Lp/\hbar$) term

$$G\left(x_f;x_i,\Delta t\right)_L=\frac{1}{2\pi\hbar}\int e^{-i\frac{\Delta t}{2m\hbar}p^2}e^{-\frac{i}{\hbar}px_i}\left\{\sum_{r=-\infty}^{+\infty}e^{2\frac{i}{\hbar}rLp}\right\}2i\underbrace{\left\{\frac{e^{\frac{i}{\hbar}px_f}-e^{-\frac{i}{\hbar}px_f}}{2i}\right\}}_{\sin\left[px_f/\hbar\right]}dp \tag{4.160}$$

while now, one recognizes, as before, the Poisson –comb function on which the similar transformation as in Eq. (4.146) holds

$$\begin{aligned}\sum_{r=-\infty}^{+\infty}e^{2\frac{i}{\hbar}prL}&=\sum_{r=-\infty}^{+\infty}e^{i2\pi r\frac{pL}{\pi\hbar}}=\sum_{n=-\infty}^{+\infty}\delta\left(\frac{pL}{\pi\hbar}-n\right)\\&=\frac{\pi\hbar}{L}\sum_{n=-\infty}^{+\infty}\delta\left(p-\frac{\pi\hbar}{L}n\right)\end{aligned} \tag{4.161}$$

This way, the propagator of the particle within the quantum well further writes from Eq. (4.160) under delta-Dirac form

$$G\left(x_f;x_i,\Delta t\right)_L=\frac{i}{L}\int e^{-i\frac{\Delta t}{2m\hbar}p^2}e^{-\frac{i}{\hbar}px_i}\sin\left[\frac{px_f}{\hbar}\right]\sum_{n=-\infty}^{+\infty}\delta\left(p-\frac{\pi\hbar}{L}n\right)dp \tag{4.162}$$

Yielding upon performing the integration by the filtration property of delta-Dirac function, see Eq. (2.11), to leave with the Green function result

$$\begin{aligned}G\left(x_f;x_i,\Delta t\right)_L=&\frac{i}{L}\sum_{n=-\infty}^{+\infty}\exp\left\{-\frac{i}{\hbar}E_n\Delta t\right\}\\&\times\exp\left\{-ik_nx_i\right\}\sin\left[k_nx_f\right]\end{aligned} \tag{4.163}$$

Where we have recorded the energy and wave vector quantifications, respectively

$$\begin{cases} E_n = \dfrac{p_n^2}{2m} = \dfrac{1}{2m}\dfrac{\pi^2\hbar^2}{L^2}n^2 \\ k_n = \dfrac{p_n}{\hbar} = \dfrac{\pi n}{L} \end{cases} \tag{4.164}$$

as driven by the delta-Dirac appearance in Eq. (4.161)

$$p_n = \frac{\pi n}{L}\hbar \tag{4.165}$$

Worth remarking that the energy quantification (4.164) for the particle trapped in the quantum wall exactly matches the earlier results (3.190a), (3.258), and (3.296), thus affirming once more the correctness of the path integral approach, while being richer in history of quantum paths' contribution.

Finally, one notes that with the quantifications in Eq. (4.164) we have also the level-properties:

$$\begin{cases} E_{-n} = E_n \\ E_{n=0} = 0 \\ k_{-n} = -k_n \end{cases} \tag{4.166}$$

With which the propagator (4.163) may be further evaluated by playing with the sum over states, i.e., by excluding the zero-state (see also the ground state solid-state paradox exposed in Section 3.5.3), while considering the remaining terms grouped under two anti-symmetrical sums:

$$\sum_{n=-\infty}^{+\infty} \bullet = \sum_{n=-\infty}^{-1} \bullet + 0 + \sum_{n=+1}^{+\infty} \bullet = \sum_{n=-1}^{+\infty} \left([\bullet]_{+n} - [\bullet]_{-n} \right) \tag{4.167}$$

to finally yield

$$G\left(x_f; x_i, \Delta t\right)_L = \frac{i}{L}\sum_{n=1}^{+\infty} \exp\left\{-\frac{i}{\hbar}E_n \Delta t\right\} 2i \underbrace{\frac{-\exp\{ik_n x_i\}}{2i}}_{-\sin[px_i/\hbar]} \sin\left[k_n x_f\right] \exp\{-ik_n x_i\}$$

$$= \frac{2}{L}\sum_{n=1}^{+\infty} \exp\left\{-\frac{i}{\hbar}E_n \Delta t\right\} \sin\left[k_n x_i\right] \sin\left[k_n x_f\right] \tag{4.168}$$

This way completing the earlier wave-function information, see for instance Eq. (3.296) or Eq. (3.596), with the actual evolution amplitude (4.168) of the quantum propagator (Green function) for electrons in the valence band of solids.

The following approach will show how the already proved quite reliable approach of path integrals is naturally needed within the Dirac formalism of quantum mechanics applied on many-particle systems, specific to chemical structures formed by many-electrons in valence state, by means of the celebrated density matrix formalism – from where there is just a step to the "observable" density functional theory of many-body systems.

4.4 DENSITY MATRIX APPROACH LINKING PATH INTEGRAL FORMALISM

4.4.1 ON MONO-, MANY-, AND REDUCED-ELECTRONIC DENSITY MATRICES

Given a spectral representation $\{|n\rangle\}_{n\in\mathrm{N}}$ for a set of quantum mono-electronic states,

$$|\varphi_k\rangle = \sum_n c_{kn}|n\rangle \tag{4.169}$$

one may employ its closure relation

$$\hat{1} = \sum_n |n\rangle\langle n| \tag{4.170}$$

to generally express the average of an observable (i.e., the operator $\hat{A}$) on a selected state as:

$$\langle \hat{A} \rangle_k = \frac{\langle \varphi_k | \hat{A} | \varphi_k \rangle}{\langle \varphi_k | \varphi_k \rangle} = \frac{\sum_{n,n'} \langle \varphi_k | n' \rangle \langle n' | \hat{A} | n \rangle \langle n | \varphi_k \rangle}{\sum_n \langle \varphi_k | n \rangle \langle n | \varphi_k \rangle} = \frac{\sum_{n,n'} c_{kn} c^*_{kn'} \langle n' | \hat{A} | n \rangle}{\sum_n |c_{kn}|^2} \tag{4.171}$$