

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

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

$$|\varphi_k\rangle = \sum_n c_{kn} |n\rangle \quad (4.169)$$

one may employ its closure relation

$$\hat{1} = \sum_n |n\rangle \langle n| \quad (4.170)$$

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

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

while for the observable average over the entire sample the individual weight w_k should be counted to provide the statistical result:

$$\langle \hat{A} \rangle = \frac{\sum_k w_k \langle \hat{A} \rangle_k}{\sum_k w_k} \quad (4.172)$$

When rewrite the global average in similar formal way as the selected k -average, actually in terms of it:

$$\langle \hat{A} \rangle = \frac{\sum_{n,n'} \langle n | \hat{\rho} | n' \rangle \langle n' | \hat{A} | n \rangle}{\sum_k w_k} \quad (4.173)$$

we introduced in fact the *density matrix elements*:

$$\langle n | \hat{\rho} | n' \rangle = \sum_k w_k \frac{c_{kn} c_{kn'}^*}{\sum_n |c_{kn}|^2} \quad (4.174)$$

which provides the *density operator*:

$$\begin{aligned} \hat{\rho} &= \sum_{n,n'} |n\rangle \langle n | \hat{\rho} | n' \rangle \langle n'| = \sum_k \frac{w_k}{\sum_n |c_{kn}|^2} \left(\sum_n c_{kn} |n\rangle \right) \left(\sum_{n'} \langle n'| c_{kn}^* \right) \\ &= \sum_k \frac{w_k}{\sum_n |c_{kn}|^2} |\varphi_k\rangle \langle \varphi_k| \end{aligned} \quad (4.175)$$

with the sum of diagonal matrix elements (the “trace” function)

$$\text{Tr} \hat{\rho} = \sum_n \langle n | \hat{\rho} | n \rangle = \sum_k w_k \frac{\sum_n |c_{kn}|^2}{\sum_n |c_{kn}|^2} = \sum_k w_k \quad (4.176)$$

while the searched operatorial average now becomes:

$$\langle \hat{A} \rangle = \frac{\sum_{n,n'} \langle n | \hat{\rho} | n' \rangle \langle n' | \hat{A} | n \rangle}{\sum_k w_k} = \frac{\sum_n \langle n | \hat{\rho} \hat{A} | n \rangle}{\sum_n \langle n | \hat{\rho} | n \rangle} = \frac{\text{Tr}(\hat{\rho} \hat{A})}{\text{Tr} \hat{\rho}} \quad (4.177)$$

Note that in above deductions the double (independent) averages technique was adopted, exploiting therefore the associate sums inter-conversions to produce the simplified results (Park et al., 1980; Blanchard, 1982; Snygg, 1982). Yet, this technique is equivalent with quantum mechanically factorization of the entire Hilbert space into sub-spaces, or at the limit into the subspace of interest (that selected to be measured, for instance) and the rest of the space being thus this approach equivalent with a system-bath sample; this note is useful for latter better understanding of the stochastic phenomena that underlay to open quantum systems, being this the physical foundation for chemical reactivity.

Next, in the case the concerned quantum states are *eigen-states*, they fulfill the normalization constraint:

$$\delta_{kk'} = \langle \varphi_k | \varphi_{k'} \rangle = \sum_n c_{kn}^* c_{k'n} \Rightarrow \sum_n |c_{kn}|^2 = 1 \quad (4.178)$$

on which base the above density operator now reads with the eigen-equation

$$\hat{\rho} | \varphi_k \rangle = \sum_{k'} w_{k'} | \varphi_{k'} \rangle \underbrace{\langle \varphi_{k'} | \varphi_k \rangle}_{\delta_{k'k}} = w_k | \varphi_k \rangle \quad (4.179)$$

leading with the eigen-values (as the diagonal elements) just the weights

$$\langle \varphi_k | \hat{\rho} | \varphi_k \rangle = w_k \quad (4.180)$$

as the observed values of the averaged density operator. Thus they have to naturally fulfill the closure probability relationship over the entire sample,

$$\sum_k w_k = 1 \quad (4.181)$$

from where the “normalization of density operator” through its above Trace property of Eq. (4.176):

$$\text{Tr} \hat{\rho} = 1 \quad (4.182)$$

Moreover, in these eigen-conditions, the operatorial average further reads from Eq. (4.177):

$$\langle \hat{A} \rangle = \text{Tr}(\hat{\rho} \hat{A}) \quad (4.183)$$

Now, there appears with better clarity the major role the density operator plays in quantum measurements, since convolutes with given operator to produce its (averaged) measured value on the prepared eigen-states. Nevertheless, when the so-called *pure states* are employed or prepared, the precedent distinction between the subsystem and system vanishes, and the density operator takes the pure quantum mechanical form of an elementary projector:

$$\hat{\rho} = |\varphi\rangle\langle\varphi| \equiv \hat{\Lambda} \quad (4.184)$$

This is a very useful expression for considering it associated with the mono-density operators when the many-fermionic systems are treated, although similar procedure applies for mixed (sample) states as well. There is immediate to see that for N formally independent partitions the Hilbert space corresponding to the N -mono-particle densities on pure states, we individually have, see Eqs. (4.176), (4.181), (4.182) and (4.184),

$$\hat{\Lambda}_i = |\varphi_i\rangle\langle\varphi_i|, \text{Tr}\hat{\Lambda}_i = 1, i = \overline{1, N} \quad (4.185)$$

producing the total operator – projector constructed by their sum

$$\hat{\Lambda}_N = \sum_{i=1}^N \hat{\Lambda}_i \quad (4.186)$$

is correctly normalized to the total number of particle:

$$\text{Tr}\hat{\Lambda}_N = \text{Tr}\left(\sum_{i=1}^N \hat{\Lambda}_i\right) = \sum_{i=1}^N \underbrace{\text{Tr}\hat{\Lambda}_i}_1 = N \quad (4.187)$$

Yet, the anti-symmetric restriction the N -fermionic state may be accounted from the mono-electronic states through considering Slater permuted (P_α) products (Putz & Chiriac, 2008; Thouless, 1972):

$$|\Phi_N\rangle = \frac{1}{\sqrt{N!}} \sum_{P_\alpha} (-1)^{P_\alpha} P_\alpha \left[\prod_{i=1}^N |\varphi_i\rangle \right] \quad (4.188)$$

for constructing the N -electronic density operator:

$$\hat{\rho}^{(N)} = |\Phi_N\rangle\langle\Phi_N| \quad (4.189)$$

with which help the $N \times N$ density matrix writes as (in coordinate representation):

$$\begin{aligned} \rho^{(N)}(x'_1 \dots x'_N; x_1 \dots x_N) &= \langle x'_1 \dots x'_N | \hat{\rho}^{(N)} | x_1 \dots x_N \rangle \\ &= \langle x'_1 \dots x'_N | \Phi_N \rangle \langle \Phi_N | x_1 \dots x_N \rangle \\ &= \frac{1}{N!} \sum_{P'_\alpha} (-1)^{P'_\alpha} P'_\alpha \left[\prod_{i=1}^N \langle x'_i | \varphi_i \rangle \right] \\ &\quad \times \sum_{P_\alpha} (-1)^{P_\alpha} P_\alpha \left[\prod_{i=1}^N \langle \varphi_i | x_i \rangle \right] \\ &= \frac{1}{N!} \sum_{P'_\alpha} (-1)^{P'_\alpha} P'_\alpha \left[\prod_{i=1}^N \varphi_i(x'_i) \right] \\ &\quad \times \sum_{P_\alpha} (-1)^{P_\alpha} P_\alpha \left[\prod_{i=1}^N \varphi_i^*(x_i) \right] \end{aligned} \quad (4.190)$$

However, in practice, due to the fact the multi-particle operators have properties associate with number of systemic properties less than the total number of particle, say of order $p < N$, worth working with the p -order *reduced density matrix* introduced as:

$$\rho^{(p)}(x'_1 \dots x'_p; x_1 \dots x_p) = \binom{N}{p} \int \Phi_N^*(x_1 \dots x_N) \Phi_N(x'_1 \dots x'_N) \prod_{j=p+1}^N dx_j \quad (4.191)$$

with the following useful properties (Blum, 1981):

- Normalization:

$$\int \rho^{(p)}(x'_1 \dots x'_p; x_1 \dots x_p) \prod_{j=1}^p dx_j = \binom{N}{p} \quad (4.192)$$

- Recursion:

$$\int \rho^{(p)}(x'_1 \dots x'_p; x_1 \dots x_p) dx_p = \frac{N+1-p}{p} \rho^{(p-1)}(x'_1 \dots x'_p; x_1 \dots x_{p-1}) \quad (4.193)$$

- First order Löwdin reduction:

$$\begin{aligned} \rho^{(p)}(x'_1 \dots x'_p; x_1 \dots x_p) &= \frac{1}{p!} \det[\rho^{(1)}(x'_k; x_k)] \\ &= \frac{1}{p!} \begin{vmatrix} \rho^{(1)}(x'_1; x_1) & \rho^{(1)}(x'_1; x_2) & \cdots & \rho^{(1)}(x'_1; x_p) \\ \rho^{(1)}(x'_2; x_1) & \rho^{(1)}(x'_2; x_2) & \cdots & \rho^{(1)}(x'_2; x_p) \\ \vdots & \vdots & & \vdots \\ \rho^{(1)}(x'_p; x_1) & \rho^{(1)}(x'_p; x_2) & \cdots & \rho^{(1)}(x'_p; x_p) \end{vmatrix} \end{aligned} \quad (4.194)$$

where the first order density matrix casts, abstracted from general definition:

$$\rho^{(1)}(x'_1; x_1) = N \int \Phi_N^*(x_1 \dots x_N) \Phi_N(x'_1 \dots x'_N) \prod_{j=2}^N dx_j \quad (4.195)$$

By these there is already noted the major importance the first order density plays in computing the higher order reduced density matrices that on their turn enters the operatorial averages, for instance:

$$\langle \hat{A} \rangle = \sum_{p=1}^N \text{Tr}^{(p)} \left[\hat{A}(x_1 \dots x_p) \hat{\rho}^{(p)} \right] \quad (4.196)$$

A special reference worth be made in regard of the free-relativist treatment of many-electronic atoms, ions, bi- or poly- atomic molecules, governed by the working Hamiltonian:

$$\hat{H} = e^2 \sum_{G < H} \frac{Z_G Z_H}{R_{GH}} + \sum_{i=1}^N \frac{p_i^2}{2m} - e^2 \sum_{i,G} \frac{Z_G}{r_{iG}} + e^2 \sum_{i < j} \frac{1}{r_{ij}} \quad (4.197)$$

those terms are represented the inter-nuclear repulsion (only for molecules), free electronic motion, electron-nuclei Coulombic attraction, and inter-electronic Coulombian repulsion, respectively. For it, the average value is computed through considering electronic density of the first or second order only there where the electronic influence is

present while the degree of matrix density is fixed by the type of electronic interaction:

$$\begin{aligned}
 \langle \widehat{H} \rangle &= e^2 \sum_{G < H} \frac{Z_G Z_H}{R_{GH}} \\
 &+ \frac{1}{2m} \int p_1^2 \rho^{(1)}(x'_1; x_1) \Big|_{x'_1=x_1} dx_1 \\
 &- e^2 \sum_G Z_G \int \frac{\rho^{(1)}(x'_1; x_1)}{r_{1G}} \Big|_{x'_1=x_1} dx_1 \\
 &+ e^2 \iint \frac{\rho^{(2)}(x'_1, x'_2; x_1, x_2)}{r_{12}} \Big|_{\substack{x'_1=x_1 \\ x'_2=x_2}} dx_1 dx_2 \quad (4.198)
 \end{aligned}$$

There is obvious that even the second order reduced matrix has appeared,

$$\rho^{(2)}(x'_1, x'_2; x_1, x_2) = \binom{N}{2} \int \Phi_N^*(x_1 \dots x_N) \Phi_N(x'_1 \dots x'_N) \prod_{j=3}^N dx_j \quad (4.199)$$

it may be further reduced to the first one through the above determinant rule:

$$\begin{aligned}
 \rho^{(2)}(x'_1, x'_2; x_1, x_2) &= \frac{1}{2!} \begin{vmatrix} \rho^{(1)}(x'_1; x_1) & \rho^{(1)}(x'_1; x_2) \\ \rho^{(1)}(x'_2; x_1) & \rho^{(1)}(x'_2; x_2) \end{vmatrix} \\
 &= \frac{1}{2} \begin{bmatrix} \rho^{(1)}(x'_1; x_1) \rho^{(1)}(x'_2; x_2) \\ -\rho^{(1)}(x'_1; x_2) \rho^{(1)}(x'_2; x_1) \end{bmatrix} \quad (4.200)
 \end{aligned}$$

emphasizing therefore on the importance of the first order reduced matrix knowledge.

The astonishing physical meaning behind this formalism relays in the fact that any multi-particle interaction (two-particle interaction included) may be reduced to the single particle behavior; in other terms, vice-versa, the appropriate perturbation (including strong-coupling) of the single particle evolution carries the equivalent information as that characterizing the whole many-body system.

In fact in this resides the power of the density matrix formalism: reducing a many-body problem to the single particle density matrix, abstracted from the single Slater determinant of Eq. (4.190) called also as *Fock-Dirac matrix*

$$\rho_{FD}^{(1)}(x'_1; x_1) = \sum_{i=1}^N \varphi_i^*(x_1) \varphi_i(x'_1) \quad (4.201)$$

and the associate operator

$$\hat{\rho}_{FD}^{(1)} = \sum_{i=1}^N |\varphi_i\rangle \langle \varphi_i| \quad (4.202)$$

that is considerably simplifying the quantum problem to be solved. Let's illustrate this by firstly quoting that Fock-Dirac density operator of Eq. (4.202) has two fundamental properties, namely:

- The idem potency:

$$\hat{\rho}_{FD}^{(1)} \hat{\rho}_{FD}^{(1)} = \sum_{i,j=1}^N |\varphi_i\rangle \langle \varphi_i | \underbrace{|\varphi_j\rangle \langle \varphi_j|}_{\delta_{ij}} = \sum_{i=1}^N |\varphi_i\rangle \langle \varphi_i| = \hat{\rho}_{FD}^{(1)} \quad (4.203)$$

- The normal additivity, see Eqs. (4.187):

$$\text{Tr} \hat{\rho}_{FD}^{(1)} = \text{Tr} \left(\sum_{i=1}^N |\varphi_i\rangle \langle \varphi_i| \right) = \text{Tr} \left(\sum_{i=1}^N \hat{\Lambda}_i \right) = N \quad (4.204)$$

while having the corresponding coordinate integral representations:

- Kernel multiplicity:

$$\int \rho_{FD}^{(1)}(x'_1; x''_1) \rho_{FD}^{(1)}(x''_1; x_1) dx''_1 = \rho_{FD}^{(1)}(x'_1; x_1) \quad (4.205)$$

- Many-body normalization:

$$\int \rho_{FD}^{(1)}(x_1; x_1) dx_1 = N \quad (4.206)$$

Remarkably, the last two identities may serve as the constraints when minimizing the above Hamiltonian average, here appropriately rewritten

employing Eqs. (4.198) and (4.200) and where all external applied potential was resumed under $V(x_1)$ under the actual so-called *Hartree-Fock trial density matrix energy functional*

$$E_{HF}[\rho_{FD}^{(1)}] = \int \left[-\frac{\hbar^2}{2m} \nabla_1^2 + V(x_1) \right] \rho_{FD}^{(1)}(x'; x_1) \Big|_{x'_1=x_1} dx_1 + \frac{e^2}{2} \iint \frac{1}{r_{12}} \left[\rho_{FD}^{(1)}(x_1; x_1) \rho_{FD}^{(1)}(x_2; x_2) - \rho_{FD}^{(1)}(x_1; x_2) \rho_{FD}^{(1)}(x_2; x_1) \right] dx_1 dx_2 \quad (4.207)$$

with the (Lagrange) variational principle:

$$\delta \left\{ \begin{array}{l} E_{HF}[\rho_{FD}^{(1)}] \\ - \iint \alpha(x'_1; x_1) \left[\int \rho_{FD}^{(1)}(x'_1; x''_1) \rho_{FD}^{(1)}(x''_1; x_1) dx''_1 \right. \\ \left. - \rho_{FD}^{(1)}(x'_1; x_1) \right] dx'_1 dx_1 \\ - \beta \left[\iint \delta(x'_1 - x_1) \rho_{FD}^{(1)}(x'_1; x_1) dx'_1 dx_1 - N \right] \end{array} \right\} = 0 \quad (4.208)$$

By the functional derivative respecting the Fock-Dirac electron density one gets:

$$\frac{\delta E_{HF}[\rho_{FD}^{(1)}]}{\delta \rho_{FD}^{(1)}(x'_1; x_1)} - \int \rho_{FD}^{(1)}(x'_1; \bar{x}) \alpha(\bar{x}; x_1) d\bar{x} - \int \alpha(x'_1; \bar{x}) \rho_{FD}^{(1)}(\bar{x}; x_1) d\bar{x} + \alpha(x'_1; x_1) - \beta \delta(x'_1 - x_1) = 0 \quad (4.209)$$

which eventually transcribes at the operatorial level:

$$\hat{F} - \hat{\rho}_{FD}^{(1)} \hat{\alpha} - \hat{\alpha} \hat{\rho}_{FD}^{(1)} + \hat{\alpha} - \beta \hat{1}_\delta = 0 \quad (4.210)$$

with $\hat{1}_\delta$ staying for the operator of the delta-Dirac matrix $\delta(x'_1 - x_1)$, while \hat{F} being the Fock operator corresponding to the coordinate matrix representation (Parr & Yang, 1989):

$$\begin{aligned}
 F(x'_1; x_1) &= \frac{\delta E_{HF} [\hat{\rho}_{FD}^{(1)}]}{\delta \hat{\rho}_{FD}^{(1)}(x'_1; x_1)} \\
 &= \left[-\frac{\hbar^2}{2m} \nabla_1^2 + V(x_1) \right] \delta(x'_1 - x_1) \\
 &\quad + \underbrace{\delta(x'_1 - x_1) e^2 \int \frac{1}{r_{12}} \rho_{FD}^{(1)}(x_2; x_2) dx_2 - \frac{e^2}{r_{11}} \rho_{FD}^{(1)}(x'_1; x_1)}_{\text{EXCHANGE CONTRIBUTION}} \quad (4.211)
 \end{aligned}$$

Equation (4.210) is most informative since, basing on the idempotency property of Eq. (4.203), through multiplying it on the right with Fock-Dirac density operator,

$$\hat{F} \hat{\rho}_{FD}^{(1)} - \hat{\rho}_{FD}^{(1)} \hat{\alpha} \hat{\rho}_{FD}^{(1)} - \hat{\alpha} \underbrace{\left(\hat{\rho}_{FD}^{(1)} \right)^2}_{\hat{\rho}_{FD}^{(1)}} + \hat{\alpha} \hat{\rho}_{FD}^{(1)} - \beta \hat{1}_\delta \hat{\rho}_{FD}^{(1)} = 0 \quad (4.212)$$

and then with the same on left side,

$$\hat{\rho}_{FD}^{(1)} \hat{F} - \underbrace{\left(\hat{\rho}_{FD}^{(1)} \right)^2}_{\hat{\rho}_{FD}^{(1)}} \hat{\alpha} - \hat{\rho}_{FD}^{(1)} \hat{\alpha} \hat{\rho}_{FD}^{(1)} + \hat{\rho}_{FD}^{(1)} \hat{\alpha} - \beta \hat{\rho}_{FD}^{(1)} \hat{1}_\delta = 0 \quad (4.213)$$

and subtracting the results, it yields:

$$\hat{F} \hat{\rho}_{FD}^{(1)} - \hat{\rho}_{FD}^{(1)} \hat{F} = 0 \quad (4.214)$$

that is equivalently of saying that Fock energy operator commutes with the Fock-Dirac density operator,

$$\left[\hat{F}, \hat{\rho}_{FD}^{(1)} \right] = 0 \quad (4.215)$$

meaning that they both admit the same set of eigen-functions. This is nevertheless the gate for obtaining the density (matrix) functional energy expressions by means of finding the density (matrix) eigen-solutions only.

Yet, condition (4.215) is indeed a workable (reduced) condition raised from optimization of the averaged Hamiltonian of a many-electronic

system, since the more general one referring to the whole Hamiltonian, known as the *Liouville or Neumann equation*, is obtained employing the temporal Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\varphi_i\rangle = \widehat{H} |\varphi_i\rangle \quad (4.216)$$

to the evolution equation of Fock-Dirac density operator evolution:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \widehat{\rho}_{FD}^{(1)} &= \sum_{i=1}^N i\hbar \frac{\partial}{\partial t} (|\varphi_i\rangle\langle\varphi_i|) = \sum_{i=1}^N i\hbar \underbrace{\left(\frac{\partial}{\partial t} |\varphi_i\rangle \right)}_{\widehat{H}|\varphi_i\rangle} \langle\varphi_i| \\ &\quad + \sum_{i=1}^N |\varphi_i\rangle \underbrace{i\hbar \left(\frac{\partial}{\partial t} \langle\varphi_i| \right)}_{\langle\varphi_i|\widehat{H}} \\ &= \widehat{H} \left(\sum_{i=1}^N |\varphi_i\rangle\langle\varphi_i| \right) - \left(\sum_{i=1}^N |\varphi_i\rangle\langle\varphi_i| \right) \widehat{H} = \left[\widehat{H}, \widehat{\rho}_{FD}^{(1)} \right] \end{aligned} \quad (4.217)$$

Lastly, note that all above properties may be rewritten since considering the *mixed p-order reduced matrix* with the form

$$\rho^{(p)}(x'_1 \dots x'_p; x_1 \dots x_p) = \sum_k w_k \rho_k^{(p)}(x'_1 \dots x'_p; x_1 \dots x_p) \quad (4.218)$$

as a natural extension of that characterizing the pure states. However, the sample statistical effects may be better considered by further expressing the electronic density operator and its matrix, equation and properties for systems in thermodynamic equilibrium (with environment), a matter in next section addressed.

4.4.2 CANONICAL DENSITY, BLOCH EQUATION, AND THE NEED OF PATH INTEGRAL

For a quantum system obeying the N -mono-electronic eigen-equations

$$\widehat{H} |\varphi_k\rangle = E_k |\varphi_k\rangle \quad (4.219)$$

the probability of finding one particle in the state $|\varphi_k\rangle$ at thermodynamical equilibrium with others, while the state + rest of states is considered a

closed supra-system with no mass or charge transfer allowed, is given by the canonical distribution (Isihara, 1980):

$$w_k = \frac{1}{Z(\beta)} \exp(-\beta E_k) \quad (4.220)$$

providing the *mixed Fock-Dirac density* with the form:

$$\begin{aligned} \hat{\rho}_N(\beta) &= \sum_{k=1}^N \frac{1}{Z(\beta)} \underbrace{\exp(-\beta E_k) |\varphi_k\rangle \langle \varphi_k|}_{\exp(-\beta \hat{H}) |\varphi_k\rangle} \\ &= \sum_{k=1}^N \frac{1}{Z(\beta)} \exp(-\beta \hat{H}) |\varphi_k\rangle \langle \varphi_k| \\ &= \frac{1}{Z(\beta)} \exp(-\beta \hat{H}) \sum_{k=1}^N |\varphi_k\rangle \langle \varphi_k| \\ &= \frac{1}{Z(\beta)} \exp(-\beta \hat{H}) \sum_{k=1}^N \left(\sum_n c_{kn} |n\rangle \right) \left(\sum_n \langle n | c_{kn}^* \right) \\ &= \frac{1}{Z(\beta)} \exp(-\beta \hat{H}) \underbrace{\sum_{k=1}^N \left(\sum_n |c_{kn}|^2 \right)}_1 \underbrace{\left(\sum_n |n\rangle \langle n| \right)}_1 \\ &= \frac{N}{Z(\beta)} \exp(-\beta \hat{H}) \end{aligned} \quad (4.221)$$

This is a very interesting and important result motivating the quantum statistical approach of determining the density of states since it corresponds to the N-sample particle throughout simple N -multiplication. Note that Eq. (4.221) is very suited for handling since its normalization factor, the partition function $Z(\beta)$, obeys the consecrated expression

$$Z(\beta) = \text{Tr} \left[\exp(-\beta \hat{H}) \right] = \int \langle x | e^{-\beta \hat{H}} | x \rangle dx \quad (4.222)$$

which is reflecting in density normalization

$$N[\rho] = \int \rho(x_1) dx_1 \quad (4.223)$$

being of paramount importance in density functional theory, the same as Eq. (4.206), because it opens the doors of observable quantities through electronic density rather than by means of wave function.

The recognized importance of partition function, in computing the internal energy as the average of the Hamiltonian of the system

$$\begin{aligned} U_N &:= \langle \widehat{H} \rangle = \text{Tr} \left[\widehat{\rho}_N(\beta) \widehat{H} \right] = \frac{N}{Z(\beta)} \text{Tr} \left[\widehat{H} \exp(-\beta \widehat{H}) \right] \\ &= -N \frac{\partial}{\partial \beta} \ln Z(\beta) \end{aligned} \quad (4.224)$$

or to evaluate the free energy of the system:

$$F_N = -N \frac{1}{\beta} \ln Z(\beta) \quad (4.225)$$

is thus transferred to the knowledge of the closed evolution amplitude $\langle x | e^{-\beta \widehat{H}} | x \rangle$, that at its turn is based on the *genuine* (not-normalized) *density operator*:

$$\widehat{\rho}_{\otimes}(\beta) = \exp(-\beta \widehat{H}) \quad (4.226)$$

sometimes called also like *canonic density operator*.

The great importance of density operator of Eq. (4.226) is immediately visualized in three ways

- It identifies the evolution operator

$$\widehat{U}(t_b, t_a) = \exp \left[-\frac{i}{\hbar} \widehat{H}(t_b - t_a) \right] \quad (4.227)$$

on the ground of Wick equivalence relationship of Eqs. (4.33) or (4.124), which allows the transformation of the Schrödinger into Heisenberg or Interaction pictures for better describing the quantum interactions;

- It produces the so-called *Bloch equation* (Bloch, 1932) by taking its β – derivative,

$$-\frac{\partial \hat{\rho}_{\otimes}(\beta)}{\partial \beta} = \hat{H} \hat{\rho}_{\otimes}(\beta) \quad (4.228)$$

that identifies with the Schrödinger equation for genuine density operator

$$i\hbar \frac{\partial}{\partial t} \hat{\rho}_{\otimes}(\beta) = \hat{H} \hat{\rho}_{\otimes}(\beta) \quad (4.229)$$

through the same Wick transformation given by Eqs. (4.33) or (4.124), thus providing the quantum-mechanically to quantum-statistical equivalence.

- Fulfills the (short times, higher temperature) so-called Markovian limiting condition:

$$\lim_{\beta \rightarrow 0} \hat{\rho}_{\otimes}(\beta) = \hat{1} \quad (4.230)$$

a very useful constraint for developing either the perturbation or the variational formalism respecting electronic density and/or partition function, see below.

In the frame of coordinate representation the Bloch problem, i.e., differential equation and its initial (Cauchy) condition, looks like:

$$\begin{cases} -\frac{\partial}{\partial \beta} \rho_{\otimes}(x'; x; \beta) = \hat{H} \rho_{\otimes}(x'; x; \beta) \\ \lim_{\beta \rightarrow 0} \rho_{\otimes}(x'; x; \beta) = \delta(x' - x) \end{cases} \quad (4.231)$$

Solution of this system is a great task in general case, unless the perturbation method is undertaken for writing the Hamiltonian a sum of a free and small interaction components,

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \quad (4.232)$$

for which the free Hamiltonian solution is completely known, say

$$\hat{\rho}_0(\beta) = \exp(-\beta \hat{H}_0) \quad (4.233)$$

In these conditions, one may firstly write:

$$\begin{aligned} \frac{\partial}{\partial \beta} \left(e^{\beta \hat{H}_0} \hat{\rho}_\otimes \right) &= \hat{H}_0 e^{\beta \hat{H}_0} \hat{\rho}_\otimes + e^{\beta \hat{H}_0} \underbrace{\frac{\partial \hat{\rho}_\otimes}{\partial \beta}}_{-\hat{H} \hat{\rho}_\otimes} = \hat{H}_0 e^{\beta \hat{H}_0} \hat{\rho}_\otimes \\ &- \left(\hat{H}_0 + \hat{H}_1 \right) e^{\beta \hat{H}_0} \hat{\rho}_\otimes = -e^{\beta \hat{H}_0} \hat{H}_1 \hat{\rho}_\otimes \end{aligned} \quad (4.234)$$

where the inter-Hamiltonian components were considered to freely commute as per wish; then, the Eq. (4.234) is integrated on the realm $[0, \beta]$ to get:

$$e^{\beta \hat{H}_0} \hat{\rho}_\otimes(\beta) - \hat{1} = - \int_0^\beta e^{\beta' \hat{H}_0} \hat{H}_1(\beta') \hat{\rho}_\otimes(\beta') d\beta' \quad (4.235)$$

rearranged under the perturbative fashion:

$$\hat{\rho}_\otimes(\beta) = \hat{\rho}_0(\beta) - \int_0^\beta \hat{\rho}_0(\beta - \beta') \hat{H}_1(\beta') \hat{\rho}_\otimes(\beta') d\beta' \quad (4.236)$$

in the form reminding by the *Lippmann-Schwinger equation* for the perturbed dynamical wave-function (Messiah, 1961), with $\hat{\rho}_0(\beta - \beta')$ playing the role of the retarded Green function $G_0(t_b - t_a)$ (Feynman, 1972). Yet, expression (4.236) may be more generalized for the p -order approximation throughout choosing various p -paths of spanning the statistical realm $[0, \beta]$ by intermediate sub-intervals:

$$\beta = \beta_{n+1} > \beta_n > \dots > \beta_2 > \beta_1 > \beta_0 = 0 \quad (4.237)$$

leading wit the expansion:

$$\begin{aligned} \hat{\rho}_\otimes(\beta) &= \hat{\rho}_0(\beta) + \sum_{l=1}^n (-1)^l \int_0^\beta d\beta_l \int_0^{\beta_l} d\beta_{l-1} \dots \int_0^{\beta_2} d\beta_1 \\ &\times \hat{\rho}_0(\beta - \beta_l) \left[\hat{H}_1(\beta_l) \hat{\rho}_0(\beta_l - \beta_{l-1}) \right] \\ &\dots \left[\hat{H}_1(\beta_2) \hat{\rho}_0(\beta_2 - \beta_1) \right] \hat{H}_1(\beta_1) \hat{\rho}_0(\beta_1) \end{aligned} \quad (4.238)$$

or in coordinate representation:

$$\begin{aligned}
 \rho_{\otimes}(x'; x; \beta) &= \rho_0(x'; x; \beta) + \sum_{l=1}^n (-1)^l \left(\int_0^{\beta} d\beta_l \int_0^{\beta_l} d\beta_{l-1} \dots \int_0^{\beta_2} d\beta_1 \right) \\
 &\quad \times \left(\int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \prod_{j=1}^l dx_j \right) \\
 &\quad \times \rho_0(x', x_l; \beta - \beta_l) \left[\widehat{H}_1(\beta_l) \rho_0(x_l; x_{l-1}; \beta_l - \beta_{l-1}) \right] \\
 &\quad \dots \left[\widehat{H}_1(\beta_2) \rho_0(x_2; x_1; \beta_2 - \beta_1) \right] \widehat{H}_1(\beta_1) \rho_0(x_1; x; \beta_1)
 \end{aligned} \tag{4.239}$$

for a parallel space discrimination of the spatial interval $[x', x]$ through the subdivisions:

$$x' = x_{n+1} > x_n > \dots > x_2 > x_1 > x_0 = x \tag{4.240}$$

Such slicing procedure in solving the Bloch equation (4.231) for canonic density solution (4.239) seems an elegant way of avoiding the self-consistent equation (4.236). Therefore, it may further employed through reconsidering the problem (4.231) in a slightly modified variant, namely within the temporal approach

$$\begin{cases} -\hbar \frac{\partial}{\partial u} \rho_{\otimes}(x'; x; u) = H(x') \rho_{\otimes}(x'; x; u) \\ \rho_{\otimes}(x'; x; u = 0) = 1 \end{cases} \tag{4.241}$$

where the variable $u = \hbar\beta$ was considered for the time dimension.

Now, in the first instance the new problem has the *formal* total solution

$$\rho_{\otimes}(x'; x; u) = \exp \left[-\frac{1}{\hbar} H(x') u \right] \tag{4.242}$$

that being of exponential type allows for direct slicing through factorization. That is, when considering the space division given by coordinate cuts of Eq. (4.240), and assuming the times flows equally on each sub-interval

in quota of ε , $u = (n+1)\varepsilon$, the density solution (4.242) may be written as a product of intermediary solutions:

$$\begin{aligned} \rho_{\otimes}(x'; x; u) &= \prod_{j=0}^{n+1} \exp\left[-\frac{1}{\hbar} H(x_j) \varepsilon\right] \\ &= \int \cdots \int \rho_{\otimes}(x'; x_l; \varepsilon) \rho_{\otimes}(x_l; x_{l-1}; \varepsilon) \cdots \rho_{\otimes}(x_1; x; \varepsilon) \prod_{j=1}^n dx_j \\ &\xrightarrow[\varepsilon \rightarrow 0]{n \rightarrow \infty} \int \cdots \int \Lambda[x(u)] Dx(u) \end{aligned} \quad (4.243)$$

$(n+1)\varepsilon = u$

where we introduced the chained covariant density product:

$$\Lambda[x(u)] = \lim_{\substack{n \rightarrow \infty \\ \varepsilon \rightarrow 0 \\ (n+1)\varepsilon = u}} \rho_{\otimes}(x'; x_l; \varepsilon) \rho_{\otimes}(x_l; x_{l-1}; \varepsilon) \cdots \rho_{\otimes}(x_1; x; \varepsilon) \quad (4.244)$$

and the extended integration metric:

$$Dx(u) = \lim_{n \rightarrow \infty} \prod_{j=1}^n dx_j \quad (4.245)$$

The general canonic solution (4.243) is called as the path integral solution for the Bloch equation (4.241), being therefore as a necessity when looking to general solutions for a given Hamiltonian. It gives general solution for electronic density (4.226) since accounting for all path connecting two end-points either in space and time (or temperatures) through in principle an infinite intermediary points; this way the resulted path integral comprises all quantum information contained by the particle' evolution between two states in thermodynamical equilibrium with environment (the other mono-particle states). However, once the canonical density evaluated through computed its path integral the associate mixed density matrix may be immediately written employing the operatorial form (4.221) to actual spatial representation

$$\rho_N(x'; x; u) = \frac{N}{Z(u)} \rho_{\otimes}(x'; x; u) \quad (4.246)$$

with the path integral based partition function written in accordance with Eq. (4.222):

$$Z(u) = \int \rho_{\otimes}(x; x; u) dx \quad (4.247)$$

while preserving the general DFT normalization condition:

$$\int \rho_N(x; x; u) dx = N \quad (4.248)$$

This way the general algorithm linking path integral to density matrix to electronic density employed by DFT for computing various density functionals (energies, reactivity indices) for characterizing chemical structure and reactivity was established, while emphasizing the basic role the path integral evaluation has in analytical evaluations towards a conceptual understanding of many-electronic quantum systems in their dynamics and interaction.

Being thus established the role and usefulness of path integral in density functional theory the next section will give more insight in appropriately defining (constructing) quantum chemical modern theories as are Hartree-Fock and density functional formalisms, being nowadays employed in various computational and conceptual schemes and applications for large classes of physico-chemical systems.

4.5 ROOTS OF SELF-CONSISTENT METHODS IN QUANTUM CHEMISTRY

Very often, the famous words of Dirac, i.e., “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known”, are quoted by theorists in physics when they like to underline that chemistry is in principle solved by the basics of quantum mechanics so that some more interesting problems should be solved. Despite this, from 1929 nowadays, quantum physics of atoms and molecules largely turns into quantum chemistry, an interdisciplinary discipline that still struggles with the elucidation of the actual behavior of electrons in nano- and bio- systems. While the total success is still not in sight, the achievements in the arsenal of concepts,