

Extended Sobolev and Hilbert spaces and approximate stationary solutions for electronic systems within the non-linear Schrödinger equation

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The definition of Sobolev spaces, which has already been shown to be a convenient way to set up the Schrödinger equation for approximate stationary solutions within extended Hilbert spaces, is readily generalized in order to express, in a similar way, the so-called non-linear Schrödinger equation (NLSE). The unavoidable theory, related to extended Hilbert and Sobolev spaces, is previously described in order to design the formalism inherent to the approximate NLSE. Afterwards the nature of the NLSE stationary solutions is discussed. The procedure uses as a basic tool an implied N -electron quantum self-similarity measure, provided with the structure of an overlap-like measure form, involving the integral of the fourth power of the N -electron wavefunction. Computation of this theoretical element is sketched and a two-electron case is developed as an illustrative example within the LCAO MO framework. The N -electron Slater determinant situation is also presented under the additional help of the nested sums formalism. It is shown afterwards that addition of second order gradient terms on the extended wavefunction provides variation of mass with velocity corrections into the energy expression. Finally, use into the Hamilton operator of exponential terms depending on the density functions in the extended Hilbert spaces formalism provides the theory with a general structure.

KEY WORDS: Sobolev spaces, extended Hilbert spaces, kinetic energy distribution, non-linear Schrödinger equation, quantum self-similarity measures, N -electron wavefunctions, nested sums formalism

1. Introduction

Actually, the definition of extended Hilbert spaces [1] has lead to several fruitful applications [2,3]. Among them one can mention a natural set-up of the Schrödinger equation within the energy expectation value approximate form, as well as the appearance of the well-known kinetic energy density [1,4,5]. Kinetic energy density can be seen, within the extended Hilbert spaces formalism as a component of a total quantum object density, involving for a given quantum object the sum of the kinetic energy density part and the particle position probability density.

Extended Hilbert spaces have been used, along with the concepts associated to the theoretical foundations of quantum similarity measures, to put into evidence the

quantum mechanical origin of the so-called quantitative structure-properties relationships (QSPR) [6–8] giving rise to the framework, which can be called quantum QSPR (QQSPR).

The most recent development of the QQSPR theory and of the subsequent applications of extended Hilbert spaces has been the evidence of their connection with Sobolev spaces [9]. The exploitation of these findings has been recently described [10], within the algorithm of SCF theory, as a procedure to solve the involved generalized secular equations.

This paper pretends to broadly re-structure the formalism of extended Hilbert spaces as well as to generalize the formal structure of Sobolev spaces. These connected possibilities will be employed afterwards to set up a stationary form of non-linear Schrödinger equation, providing at the same time the way to obtain approximate solutions within the well-known LCAO MO framework. Finally, it will be shown that addition of more second order terms in the extended wavefunction framework produces a non-linear Schrödinger equation whose energy expression includes variation of mass with the energy expectation values.

2. Extended Hilbert spaces

The main idea leading to the construction of extended Hilbert spaces has been latent in the usual quantum mechanical postulates, associated to the wavefunction definition and properties, since the dawn of quantum mechanics [11]. Certainly, in this respect the quantum mechanical wavefunctions, as solutions of Schrödinger equation, shall behave properly and essentially as such, they shall form part of square sumable functions [12,13]. However, the first derivatives of quantum mechanical wavefunctions should also possess the same properties as their original counterparts have. Thus, the wavefunction and their gradients must be taken, in this sense, on the same footing, while being independent one from another.

2.1. Structure of extended Hilbert spaces

These wavefunction characteristics, when gradients are to be taken into account as well as the bulk functions themselves, originated the idea of extended Hilbert spaces. The definition of an extended Hilbert space can be cast as follows. Suppose a stationary wavefunction, $\Psi(\mathbf{r})$, of some state of a known N -particle quantum object. Then, the vector \mathbf{r} has to contain the coordinates of the positions associated to the quantum object particles. Suppose that the gradient of such wavefunction is symbolized by $\nabla\Psi(\mathbf{r})$. An element of the extended Hilbert space can be defined as the ket vector of the appropriate dimensions:

$$\Phi(\mathbf{r}) = \begin{pmatrix} \Psi(\mathbf{r}) \\ \nabla\Psi(\mathbf{r}) \end{pmatrix} \equiv \begin{pmatrix} \Psi \\ \nabla\Psi \end{pmatrix} = \Phi \equiv |\Phi\rangle. \quad (1)$$

The Hilbert norm [14; 15, pp. 420, 422; 16, p. 6; 17; 18, p. 334] of the extended wavefunctions, which can be interpreted as follows:

$$\langle \Phi | \Phi \rangle = \langle \Psi | \Psi \rangle + \langle \nabla \Psi | \nabla \Psi \rangle = 1 + 2\langle \mathbf{K} \rangle,$$

where the system wavefunction Ψ is supposed to be normalized:

$$\langle \Psi | \Psi \rangle = 1,$$

and the symbol $\langle \mathbf{K} \rangle$, associated to the following integrals:

$$\frac{1}{2} \langle \nabla \Psi | \nabla \Psi \rangle = -\frac{1}{2} \langle \Psi | \nabla^2 | \Psi \rangle = \langle \mathbf{K} \rangle$$

is the expectation value of the quantum mechanical kinetic energy of the system under study.

2.2. Sobolev spaces

The resultant structure of the extended Hilbert space norms can be associated to the usual form of a Sobolev space [19, p. 379]. In Sobolev spaces [9], the norm of any of their elements, Ψ say, is defined within a general formulation as

$$\|\Psi\|_n^m = \sum_{p=0}^m \|\nabla^p \Psi\|_n, \quad (2)$$

where the first term of the sum in equation (2) has to be considered as a way to write the bulk wavefunction:

$$\nabla^0 \Psi \equiv \Psi. \quad (3)$$

It is obvious that the extended Hilbert space functions from the point of view of the above-defined norms can be considered a Sobolev space with the norm defined as:

$$\langle \Phi | \Phi \rangle \equiv \|\Psi\|_2^1. \quad (4)$$

3. Generalized Sobolev spaces

A trivial generalization of Sobolev spaces can be readily described, taking as a starting point the extended Hilbert spaces as defined above. Suppose that the Sobolev definition (2) can be generalized in such a way that it can be written, among other possibilities as

$$\|\Psi\|_n^{r;s} = \sum_{p=1}^r \|\Psi\|^p + \sum_{q=1}^s \|\nabla^q \Psi\|_n. \quad (5)$$

In a symmetrical way with the first term in equation (5), there can be also defined the following norm:

$$\|\Psi\|_n^{r;s;t} = \sum_{p=1}^r \|\Psi^p\|_n + \sum_{k=1}^t \sum_{q=1}^s \|\nabla^q \Psi^k\|_n. \quad (6)$$

So, in fact, equation (6) transforms into (5), when $t = 1$, in the same way as equation (5) transforms into the original Sobolev definition (2) when $r = 1$.

Taking this into account and the conventional meaning of the zeroth order gradient symbol, as already described in equation (2), one can first try to reach an extended Hilbert space whose functions can be associated to a generalized Sobolev space (5) with the following norm structure:

$$\langle \Phi | \Phi \rangle \equiv \|\Psi\|_2^{2;1} = \|\Psi\|_2 + \|\Psi^2\|_2 + \|\nabla \Psi\|_2.$$

So, there may be written a new vector form of the extended wavefunctions as a three-dimensional column matrix

$$|\Phi\rangle = \begin{pmatrix} \Psi \\ |\Psi|^2 \\ \nabla \Psi \end{pmatrix} = \begin{pmatrix} \Psi \\ \rho \\ \nabla \Psi \end{pmatrix}, \quad (7)$$

taking into account that the density function ρ in the expression (7) is the squared module of the initial wavefunction form. The explicit extended function norm will be written now as

$$\langle \Phi | \Phi \rangle = 1 + \langle \rho | \rho \rangle + 2\langle \mathbf{K} \rangle. \quad (8)$$

The Hilbert norm of the total density form appears in equation (8) as another term in the extended Hilbert space norm. The new positive definite term corresponds to an integral with the form

$$\langle \rho | \rho \rangle = \int \rho^2 \, d\mathbf{r} = \langle |\Psi|^2 | |\Psi|^2 \rangle = \int |\Psi|^4 \, d\mathbf{r}. \quad (9)$$

Such kind of integrals is well known in the field of quantum similarity and corresponds to a quantum self-similarity overlap-like measure [3] involving the N th order density matrices.

4. Non-linear Schrödinger equation generated throughout extended Hilbert space wavefunctions

4.1. Classical Schrödinger energy expression from extended wavefunctions

The extended wavefunction form (1) can be used with the appropriately modified Hamilton operator in order to obtain the system's energy expectation value [1]; for an application to a generalized form of Hohenberg–Kohn theorem, see, for example, [20].

In order to arrive at this expression, the Hamilton operator could be written as a diagonal matrix with the form

$$\mathbf{H} = \begin{pmatrix} \mathbf{V} & 0 \\ 0 & \frac{1}{2}I \end{pmatrix} = \text{Diag}\left(\mathbf{V}; \frac{1}{2}I\right), \quad (10)$$

where \mathbf{V} is the potential operator and I an appropriate dimension unit operator. Taking into account the definition (10) and the extended wavefunction structure in equation (1), the energy expression is obtained in a quantum mechanical expectation value form

$$\begin{aligned} E &= \langle \Phi | \mathbf{H} | \Phi \rangle = \langle \Psi | \mathbf{V} | \Psi \rangle + \frac{1}{2} \langle \nabla \Psi | \nabla \Psi \rangle \\ &= \langle \mathbf{V} \rangle + \langle \mathbf{K} \rangle \\ &= \int V \rho \, d\mathbf{r} + \frac{1}{2} \int |\nabla \Psi|^2 \, d\mathbf{r} \end{aligned} \quad (11)$$

but readily expressible within a statistical density probability function integral structure. This is obvious for the potential part and elementary to see that for kinetic energy holds the same, as the square module of the wavefunction gradient can be considered too as a kinetic energy density function, using the simple definition

$$\kappa(\mathbf{r}) = |\nabla \Psi(\mathbf{r})|^2. \quad (12)$$

This last equality also permits to construct a total or extended density function starting from the usual way to construct density functions from general well-behaved functions

$$\tau(\mathbf{r}) = |\Phi|^2 = |\Psi|^2 + |\nabla \Psi|^2 = \rho(\mathbf{r}) + \kappa(\mathbf{r}).$$

4.2. Energy expression from generalized extended wavefunctions

If one takes into account the alternative extended wavefunction (7), then the appropriate Hamiltonian to be used here, in order to write an energy-like expectation value, has to be constructed in a similar way as the diagonal operator (10), just taking into account the extra functional term in the wavefunction (7)

$$\mathbf{H}_\alpha = \begin{pmatrix} \mathbf{V} & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \frac{1}{2}I \end{pmatrix} = \text{Diag}\left(\mathbf{V}; \alpha; \frac{1}{2}I\right), \quad (13)$$

where only a scalar value $\alpha \in \mathbb{R}$, is added [21]. As in the Hamiltonian expectation value expression (11), the operator (13) with the wavefunction (7) will produce the energy-like

form:

$$\begin{aligned}
 E_\alpha &= \langle \Phi | \mathbf{H}_\alpha | \Phi \rangle \\
 &= \langle \mathbf{V} \rangle + \alpha \langle \Psi | \rho | \Psi \rangle + \langle \mathbf{K} \rangle \\
 &= \langle \Psi | \mathbf{H} | \Psi \rangle + \alpha \langle \Psi | \rho | \Psi \rangle \\
 &= E + \alpha \langle \rho | \rho \rangle.
 \end{aligned} \tag{14}$$

In the resultant ending expression, E is the expectation value as discussed in equation (11), while the last term corresponds to the overlap-like self-similarity over the N th order density function as commented in equation (9).

This result will be obvious if it could not be associated with the Hamiltonian operator of the so-called non-linear Schrödinger equation. See for an excellent review on this subject the book of Fraga et al. [21]. In such an equation, to the usual Hamilton operator of the linear Schrödinger equation it is added the density function multiplied by a real scalar factor. Thus, in the same manner as equation (11) corresponds to the energy expectation value of the linear Schrödinger equation, to the equation (14) one can attach the form of the energy expectation value associated to a stationary non-linear Schrödinger equation.

In this formalism, the unique difference between both linear and non-linear equations corresponds to the presence of the overlap-like self-similarity term and so, variation of expression (14) will coincide with expression (11), but the integral $\langle \rho | \rho \rangle$ shall be taken into account. A self-similarity term can be interpreted in several ways [3], however, in the present case it could be seen as the expectation value of the density function itself, which can be considered as a distribution and as a projection operator as well, that is

$$\langle \rho | \rho \rangle = \langle \rho \rangle.$$

5. Two-electron system case as an example

5.1. Introduction

Owing to the fact that in the stationary non-linear Schrödinger equation one only has to take into account the overlap-like self-similarity variation, then at first glance there it seems that approximate solutions in the non-linear case could be readily obtained. Self-similarity and more complex overlap-like measures involving two or more quantum objects have been described in many instances; for more details see, e.g., [3]. However, the similarity measures involved in these previous theoretical findings and their applications are mainly associated to first and second order density functions. There must be kept in mind that the self-similarity integral $\langle \rho | \rho \rangle$, as considered in this work, which is nothing more than a norm in a Hilbert semispace [3], shall be computed over the density function of N th order. Because of this, electronic quantum objects will present an added difficulty due to the presence of spin.

The presence of spin can produce a very complicated algorithmic pattern, even in the most elementary two-electron case, studied within an approximate monoconfigurational wavefunction in a standard LCAO-MO model. However, such a theoretical study could be illustrative enough as to merit to be commented as a first example of approximate solutions of the non-linear Schrödinger equation.

Some years ago a study of an approximate CI procedure has been described in our laboratory, employing a two-electron wavefunction structure as an example [22] and the experience was sufficient to prove the properties of the algorithm. So, it seems that a starting point to study the introduction of non-linear terms in the usual calculations with such elementary systems is not so unrealistic, as it could be thought at first glance. The following discussion will demonstrate that the expected problems appear even at this elementary stage.

5.2. Two-electron closed shell LCAO-MO monodeterminantal case

5.2.1. Spin density treatment

Suppose that a normalized MO $\psi(\mathbf{r})$ is known, sufficiently accurate for describing the ground state of a two-electron system, then the associated monodeterminantal wavefunction can be written as

$$\Psi(\mathbf{r}_1; \mathbf{r}_2) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)\Sigma_1(1; 2),$$

where the two-electron singlet spin wavefunction part can be written using the well-known expression

$$\Sigma_1(1; 2) = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}. \quad (15)$$

In the equation (15), the function pair $\{\alpha; \beta\}$ is made by the usual spin-functions depending on the *spin coordinates* of the involved pair of electrons. The two-electron global density function can be separated in the usual space and spin parts as follows:

$$\rho(1; 2) = |\Psi(1; 2)|^2 = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)|\Sigma_1(1, 2)|^2,$$

where $\rho(\mathbf{r}_i) = |\psi(\mathbf{r}_i)|^2$, and the spin density part will be easily developed in the following four terms:

$$\begin{aligned} |\Sigma_1(1; 2)|^2 = \frac{1}{2} \{ & |\alpha(1)|^2|\beta(2)|^2 - (\alpha(1)^*\beta(1))(\beta(2)^*\alpha(2)) \\ & - (\beta(1)^*\alpha(1))(\alpha(2)^*\beta(2)) + |\beta(1)|^2|\alpha(2)|^2 \}. \end{aligned} \quad (16)$$

The real problem appears when the integral of the two-electron spin density function (16) has to be obtained over the two spin coordinates in the following way:

$$\langle |\Sigma_1|^2 || \Sigma_1|^2 \rangle = \iint |\Sigma_1(1, 2)|^2 |\Sigma_1(1, 2)|^2 ds_1 ds_2. \quad (17)$$

5.2.2. Integrals involving four spin-functions

It is then easy to see that integrals involving *four* spin-functions and a *unique* spin coordinate may appear when trying to obtain the result of the integral (17). These integrals can be written in the generic form

$$\langle \sigma_a \sigma_b | \sigma_c \sigma_d \rangle = \int \sigma_a^*(s) \sigma_b(s) \sigma_c^*(s) \sigma_d(s) ds, \quad (18)$$

where the spin-functions $\{\sigma_p(s)\}$ can be any combination of the $\{\alpha; \beta\}$ spin-function pair associated to the *same* spin coordinate. The four spin-functions integral (18) can be also obviously written into the following equivalent way:

$$\begin{aligned} \langle \sigma_a \sigma_c : \sigma_b \sigma_d \rangle &= \int \sigma_a^*(s) \sigma_c^*(s) \sigma_b(s) \sigma_d(s) ds \\ &= \int (\sigma_a(s) \sigma_c(s))^* \sigma_b(s) \sigma_d(s) ds. \end{aligned} \quad (19)$$

The integral (19) can be now seen as a scalar product between the four possible products of two spin-functions, that is the same as to say any element of the set: $\{\alpha\alpha; \alpha\beta; \beta\alpha; \beta\beta\}$. It should be noted again that the involved functions in the integral (19) must be associated to the *same* spin-variable. In order to see what shall be the resultant value of the set of integrals (19), one can take into account that the scalar product integrals between any pair of spin-functions can be written, employing a logical Kronecker delta [23]

$$\langle \sigma_a | \sigma_b \rangle = \int \sigma_a^*(s) \sigma_b(s) ds = \delta(\sigma_a = \sigma_b),$$

which is the same to say that the $\{\alpha; \beta\}$ spin-function pair forms an orthonormalised basis set. It can be easily seen [13] that the corresponding two spin function orthonormalised products are reduced to the set $\{\alpha\alpha; \sqrt{2}\alpha\beta; \beta\beta\}$, and this situation induces the following result for the integrals (19)

$$\begin{aligned} \langle \sigma_a \sigma_c : \sigma_b \sigma_d \rangle &= \delta[(\sigma_a = \sigma_b \wedge \sigma_c = \sigma_d) \vee (\sigma_a = \sigma_d \wedge \sigma_c = \sigma_b)] \\ &\quad \times \{1 + \delta(\sigma_a \neq \sigma_c)\}^{-1}, \end{aligned} \quad (20)$$

where the logical Kronecker delta symbol has been employed again. This result implies that when integrals involving two products, made of two spin-functions themselves, are to be integrated over the same spin variable, the result is null excepting if both involved spin-function within the products are the same.

5.2.3. The self-similarity measure integral

Thus, the integral (17) has the final simple value

$$\langle |\Sigma_1|^2 | |\Sigma_1|^2 \rangle = \frac{3}{4},$$

which tells that two-electron singlet spin-density functions can be easily normalized under the present definition of the spin function norm. For this one can use a new normalized spin-density function

$$|\Sigma_1|_N^2 = \frac{2}{\sqrt{3}}|\Sigma_1|^2,$$

and from there a unit spin self-similarity integral is obtained:

$$\langle |\Sigma_1|_N^2 | |\Sigma_1|_N^2 \rangle = 1. \quad (21)$$

These considerations allow the evaluation of the total two-electron self-similarity integral as the square of an overlap self-similarity over the MO space, as

$$\begin{aligned} \langle \rho(1; 2) | \rho(1; 2) \rangle &= \left(\int |\rho(\mathbf{r}_1)|^2 d\mathbf{r}_1 \right) \left(\int |\rho(\mathbf{r}_2)|^2 d\mathbf{r}_2 \right) \\ &= \left(\int |\rho(\mathbf{r})|^2 d\mathbf{r} \right)^2 \\ &= \left(\int |\psi^*(\mathbf{r})\psi(\mathbf{r})|^2 d\mathbf{r} \right)^2 \\ &= \theta^2. \end{aligned} \quad (22)$$

Equation (22) indicates that the self-similarity measure associated to the density function computed in a monodeterminantal-closed shell two-electron system coincides with the square of the MO self-similarity measure.

5.3. Non-linear self consistent field (NL-SCF) theory for closed shell two-electron systems

The result found above makes easy to write the non-linear energy expression, which will be written as equation (14), but taking into account equation (22):

$$E_\alpha = E + \alpha\theta^2. \quad (23)$$

The subsequent variation of equation (23) leads to the definition of the Fock operator for the linear energy part:

$$F = h + J,$$

where h is the mono-electronic Hamiltonian and J the Coulomb operator. The non-linear Fock operator can thus be written as

$$F_\alpha = F + \alpha\theta Z,$$

where α is the non-linear parameter, including the variational constant factors related to the self-similarity integral variation, θ is the self-similarity integral over the MO $\psi(\mathbf{r})$, as defined in equation (22), and finally Z is a density operator, such that

$$\theta = \langle \psi | Z | \psi \rangle = \int \psi(\mathbf{r})^* Z(\mathbf{r}) \psi(\mathbf{r}) \, d\mathbf{r}.$$

5.4. Excited singlets and triplets of two-electron systems

In the same way as done in the closed shell two-electron case, there appears no other problem than the one associated to the self-similarity handling, when dealing with the possible two-electron excited open shells.

5.4.1. Excited open shell singlets

The excited open shell singlet case can be immediately studied, as the spin part of the self-similarity is the same as in the former closed shell case. The MO density part has a particular theoretical different flavor, as two different space orbitals shall be taken into account $\{\psi_p; \psi_q\}$, say.

The two-electron wavefunction will be written in this case as

$$\Psi_S(\mathbf{r}_1; \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \psi_p(\mathbf{r}_1) \psi_q(\mathbf{r}_2) + \psi_q(\mathbf{r}_1) \psi_p(\mathbf{r}_2) \} \Sigma_1(1; 2).$$

Then, assuming the same spin contribution as in equation (21), the excited singlet space density will be formed by four terms:

$$\rho_S(\mathbf{r}_1; \mathbf{r}_2) = \frac{1}{2} \{ \rho_{pp}(1) \rho_{qq}(2) + \rho_{pq}(1) \rho_{qp}(2) + \rho_{qp}(1) \rho_{pq}(2) + \rho_{qq}(1) \rho_{pp}(2) \},$$

where the MO densities are described as

$$\rho_{ij}(k) = \psi_i^*(\mathbf{r}_k) \psi_j(\mathbf{r}_k) \quad (24)$$

with $i, j \in \{p, q\}$ and $k \in \{1, 2\}$. In these circumstances the two-electron space self-similarity, taking into account the possible complex values of the four involved MO, can be written as

$$\theta_S = \frac{1}{2} \{ (pp \| pp)(qq \| qq) + 4\text{Re}((pp \| pq)(qq \| qp)) + (pp \| qq)^2 + |(pq \| pq)|^2 + (pq \| qp)^2 \},$$

where the involved integrals over the active MO are defined as

$$(ij \| kl) = \int \rho_{ij}(\mathbf{r}) \rho_{kl}(\mathbf{r}) \, d\mathbf{r},$$

employing the previous MO densities as defined in equation (24). With real MO functions, which is the most usual case, the self-similarity becomes

$$\theta_S = \frac{1}{2} \{ (pp \| pp)(qq \| qq) + 4(pp \| pq)(pq \| qq) + 3(pp \| qq)^2 \}.$$

5.4.2. Excited triplets

In the triplet case, a similar treatment can be performed as in the previous one. The triplet wavefunction can be written as

$$\Psi_{\text{T}}(\mathbf{r}_1; \mathbf{r}_2) = \frac{1}{\sqrt{2}} \{ \psi_p(\mathbf{r}_1)\psi_q(\mathbf{r}_2) - \psi_q(\mathbf{r}_1)\psi_p(\mathbf{r}_2) \} \Sigma_3(1; 2),$$

and

$$\Sigma_3(1; 2) = \alpha(1)\alpha(2).$$

The triplet spin-density self-similarity integral will yield a unity result, according to the values of spin-density integrals (20). The argument to show this becomes in the triplet case still more trivial than in the singlet, so it will not be further discussed. The space density will be also trivially obtained, as the function

$$\rho_{\text{T}}(\mathbf{r}_1; \mathbf{r}_2) = \frac{1}{2} \{ \rho_{pp}(1)\rho_{qq}(2) - \rho_{pq}(1)\rho_{qp}(2) - \rho_{qp}(1)\rho_{pq}(2) + \rho_{qq}(1)\rho_{pp}(2) \},$$

so, employing the same arguments as in the excited singlet case the corresponding two-electron self-similarity measure may be written as

$$\begin{aligned} \theta_{\text{T}} = \frac{1}{2} \{ & (\rho_{pp}\|\rho_{pp})(\rho_{qq}\|\rho_{qq}) - 4\text{Re}[(\rho_{pp}\|\rho_{pq})(\rho_{qq}\|\rho_{qp})] \\ & + (\rho_{pp}\|\rho_{qq})^2 + |(\rho_{pq}\|\rho_{pq})|^2 + (\rho_{pq}\|\rho_{qp})^2 \}, \end{aligned}$$

which in the real MO case will be simplified to the form

$$\theta_{\text{T}} = \frac{1}{2} \{ (\rho_{pp}\|\rho_{pp})(\rho_{qq}\|\rho_{qq}) - 4(\rho_{pp}\|\rho_{pq})(\rho_{pq}\|\rho_{qq}) + 3(\rho_{pp}\|\rho_{qq})^2 \}.$$

Owing to the normalized condition of both state spin self-similarities, the singlet-triplet difference between both measures in is easily obtained to be

$$\Delta\theta = \theta_{\text{S}} - \theta_{\text{T}} = 4\text{Re}[(\rho_{pp}\|\rho_{pq})(\rho_{qq}\|\rho_{qp})].$$

6. Many-electron wavefunctions and self-similarity measures

It appears from the previous two-electron discussion, that the main problem in the approximate solution of the non-linear Schrödinger equation is the handling of the self-similarity integrals over spin-density functions. Thus, the N -electron case will be worth of some analysis. In order to ease the Slater determinant manipulation, the simple expression of such N -electron wavefunctions issuing from the nested sum symbols [23] formalism, proposed by us several years ago, will be employed here.

A unnormalized Slater determinant wavefunction can be written in terms of the N spin-orbital set $\{\phi_i\}$ employing the nested summation symbol formalism as follows:

$$\Phi(1, 2, \dots, N) = \text{Det}|\phi_1, \phi_2, \dots, \phi_N| = \sum_N(\mathbf{i})\Omega(\mathbf{i})\phi(\mathbf{i}), \quad (25)$$

where the nested summation symbol: $\sum_N(\mathbf{i})$ describes in a condensed way a nested sequence of N summation symbols, generating all the possible values of the indices in every sum and collecting the indices at every step within an N -dimensional index vector \mathbf{i} ; $\Omega(\mathbf{i})$ is a filter present in order to select, among all the generated index vectors, those which are a permutation of the canonical index order and at the same time delivers the corresponding permutation signature, according to the situation where the index vector corresponds to even or odd permutations. Finally, the symbol

$$\phi(\mathbf{i}) = \phi_{i_1}(1)\phi_{i_2}(2)\cdots\phi_{i_N}(N) = \prod_{k=1}^N \phi_{i_k}(k) \quad (26)$$

can be taken as a product of a permutation of the spin-orbitals, while conserving the one-electron space and spin coordinates in the canonical order. This final product may be conveniently written separating the space MO functions from the spin-functions, as

$$\phi(\mathbf{i}) = \psi(\mathbf{i})s(\mathbf{i}), \quad (27)$$

with a similar expression as in equation (26), for each space and spin parts of (27). Such nested summation sum formalism permits to obtain a neat expression for the density function attached to any Slater determinant, which taking into account the expressions (25), (26) and (27), can be easily expressed as

$$\rho(1, 2, \dots, N) = \sum_N(\mathbf{i}) \sum_N(\mathbf{j}) \Omega(\mathbf{i}) \Omega(\mathbf{j}) \psi(\mathbf{i})^* \psi(\mathbf{j}) s(\mathbf{i})^* s(\mathbf{j}). \quad (28)$$

So, one can see that in the self-similarity integral involving the density as expressed in equation (28), every term of the double nested summation symbol may be easily separated into the space and spin integration. More than this: in every term involving the square of the density function (28), the spin part can be seen also separable among the integrals concerning four spin-functions and integrated over only one spin-variable, yielding products of N integrals, which every term will be exactly equivalent to the ones described in the two-electron case, as expressed in equation (19). Because of the orthonormalisation relationships exported from the spin-functions into the pairs of spin-function products, the final expression of the self-similarity integral, involving the density function (28) will be thus greatly simplified.

In this manner, the self-similarity integral for an arbitrary many-electron Slater determinant can be written as

$$\begin{aligned} \theta &= \sum_N(\mathbf{i}) \Omega(\mathbf{i}) \sum_N(\mathbf{j}) \Omega(\mathbf{j}) \sum_N(\mathbf{k}) \Omega(\mathbf{k}) \sum_N(\mathbf{l}) \Omega(\mathbf{l}) \\ &\times \int \psi(\mathbf{i}) \psi(\mathbf{j})^* \psi(\mathbf{k})^* \psi(\mathbf{l}) d\mathbf{X} \cdot \int s(\mathbf{i}) s(\mathbf{j})^* s(\mathbf{k})^* s(\mathbf{l}) ds. \end{aligned} \quad (29)$$

According to an immediate generalization of equation (20) the spin part integration can be expressed as

$$\int s(\mathbf{i})s(\mathbf{j})^*s(\mathbf{k})^*s(\mathbf{l}) \, ds = \langle s(\mathbf{j})s(\mathbf{k}) : s(\mathbf{i})s(\mathbf{l}) \rangle = \delta[(\mathbf{i} = \mathbf{j} \wedge \mathbf{k} = \mathbf{l}) \vee (\mathbf{i} = \mathbf{k} \wedge \mathbf{j} = \mathbf{l})] \Delta(\mathbf{j} \neq \mathbf{k}), \quad (30)$$

where a new symbol is needed:

$$\Delta(\mathbf{j} \neq \mathbf{k}) = \left(\prod_i (1 + \delta(j_i \neq k_i)) \right)^{-1}.$$

Among the vectors $\mathbf{i}, \mathbf{j}, \mathbf{k}$ and \mathbf{l} always two pairs of equalities are established. That is due to the conditions imposed by the logical Kronecker symbols. In this way, the eventual negative signs arising from the Ω coefficients disappear and, finally,

$$\begin{aligned} \theta &= \sum_N(\mathbf{i}) \sum_N(\mathbf{j}) \sum_N(\mathbf{k}) \sum_N(\mathbf{l}) \cdot P(\mathbf{i})P(\mathbf{j})P(\mathbf{k})P(\mathbf{l}) \\ &\quad \times \delta[(\mathbf{i} = \mathbf{j} \wedge \mathbf{k} = \mathbf{l}) \vee (\mathbf{i} = \mathbf{k} \wedge \mathbf{j} = \mathbf{l})] \Delta(\mathbf{j} \neq \mathbf{k}) \\ &\quad \times \int \psi(\mathbf{i})\psi(\mathbf{j})^*\psi(\mathbf{k})^*\psi(\mathbf{l}) \, d\mathbf{X}, \end{aligned} \quad (31)$$

where the terms $P(\mathbf{i})$ are filters, choosing from all the possible index vectors the ones representing permutations without signature.

Finally, it must be taken into account that the Slater determinant function has been used unnormalized, so the final expression (31) shall be corrected by the appropriate fourth power of the normalization factor $(1/\sqrt{N!})$.

7. Extended non-linear Schrödinger equation

When observing the structure of the non-linear form of both the Hamilton operator and the extended wavefunction, one can easily propose a symmetrical extended Schrödinger equation with respect to the wavefunction and their gradient powers. This will correspond not only to the presence of a second order wavefunction term, a density function term appearing in the system Hamiltonian, but owing to the kinetic energy interpretation as given in equation (12), one can construct a similar term with respect to the kinetic energy to be used in the extended wavefunction. This can be obtained throughout an extended Sobolev space as defined in equation (6), with a norm particularly defined for this case as

$$\langle \Phi | \Phi \rangle \equiv \|\Psi\|_2^{2;1;2} = \|\Psi\|_2 + \|\Psi^2\|_2 + \|\nabla\Psi\|_2 + \|\nabla\Psi^2\|_2,$$

which will correspond to a possible four-dimensional extended wavefunction, that could be expressed, in turn, as

$$|\Phi\rangle = \begin{pmatrix} \Psi \\ |\Psi|^2 \\ \nabla\Psi \\ |\nabla\Psi|^2 \end{pmatrix} \equiv \begin{pmatrix} \Psi \\ \rho \\ \nabla\Psi \\ \kappa \end{pmatrix}. \quad (32)$$

Here κ is the kinetic energy density, as defined in equation (12), and in this manner the corresponding diagonal Hamilton operator could be written just as the non-linear Hamiltonian discussed so far, and described in equation (13) with an extra term

$$\mathbf{H}_{\alpha;\beta} = \begin{pmatrix} \mathbf{V} & 0 & 0 & 0 \\ 0 & \alpha & 0 & 0 \\ 0 & 0 & I/2 & 0 \\ 0 & 0 & 0 & \beta \end{pmatrix} = \text{Diag}(\mathbf{V}; \alpha; I/2; \beta), \quad (33)$$

where the parameter $\beta \in \mathbb{R}$ can be used in the same footing as the former non-linear term α was defined.

Alternatively, there are also other possibilities, which can be associated to the parameter β .

The first one corresponds to the geometrical nature of the kinetic energy density. In some discussion about the extended wavefunction (1) and the corresponding total density function [1–3], it was proposed the construction of a convex mixture of the space and kinetic energy densities. In this proposal, if the parameter $\omega \in [0, 1]$ is defined, then a composite density can be obtained with the simple form

$$\gamma(\mathbf{r}) = \omega\rho(\mathbf{r}) + (1 - \omega)\kappa(\mathbf{r}).$$

Some visual examples of this density convex mixture can be obtained from [1]. Thus, from this point of view the non-linear parameters can be taken as convex coefficients and chosen in the Hamiltonian (33) accordingly, for example, using $\alpha \in [0, 1]$ and $\beta = 1 - \alpha$.

A physical interpretation of both the non-linear parameter β and the possibly connected extended energy term is somehow related to the variation of mass with velocity in the Breit Hamiltonian [24–28]. Indeed, if the associated energy in the present extended wavefunction (32) and Hamiltonian (33) is obtained in the same way as in the other previously studied cases, the following expression appears:

$$\begin{aligned} E_{\alpha;\beta} &= \langle \Phi | \mathbf{H}_{\alpha;\beta} | \Phi \rangle = E_{\alpha} + \beta \langle |\nabla\Psi|^2 | |\nabla\Psi|^2 \rangle \\ &= E_{\alpha} + \beta \langle \kappa | \kappa \rangle, \end{aligned}$$

so the last term, owing to the similarity with the Breit Hamiltonian interpretation can be supposedly multiplied by a corresponding constant composed with equivalent units [26–28]. The resultant integral form of the similar Breit term corresponds to the norm of the kinetic energy density function, or employing quantum similarity terminology, this term is a self-similarity measure involving the kinetic energy density distrib-

ution. It is structured in a similar norm form to the one Bethe and Salpeter [24] recommend computing the variation of mass with velocity integral, as it will be discussed below. However, one can insist in the fact that the extra term in this extended non-linear Schrödinger equation energy expression can be also described as a kinetic energy distribution self-similarity, owing to the related structure of the previously discussed spatial density function term as included in the energy E_α , as shown in equation (22).

The exact form of the Breit Hamiltonian term, associated to the variation of the mass with velocity, can be obtained by means of a Sobolev space of the kind related to the norms defined in equation (5). Indeed, using the Sobolev norm:

$$\langle \Theta | \Theta \rangle \equiv \|\Psi\|_2^{2;2} = \|\Psi\|_2 + \||\Psi|^2\|_2 + \|\nabla\Psi\|_2 + \|\nabla^2\Psi\|_2,$$

then, to this extended Sobolev norm one can attach the following extended wavefunction:

$$|\Theta\rangle = \begin{pmatrix} \Psi \\ |\Psi|^2 \\ \nabla\Psi \\ \nabla^2\Psi \end{pmatrix} \equiv \begin{pmatrix} \Psi \\ \rho \\ \nabla\Psi \\ \Delta\Psi \end{pmatrix},$$

which can be used with the same Hamilton operator (33) as in the previous case, yielding the energy form

$$E_{\alpha;\beta}^{(\Theta)} = \langle \Theta | \mathbf{H}_{\alpha;\beta} | \Theta \rangle = E_\alpha + \beta \langle \Delta\Psi | \Delta\Psi \rangle,$$

which has the Breit correction in the appropriate form recommended by Bethe and Salpeter [24]. Therefore, in this situation, the corresponding parameter β has the true meaning of the mass variation with velocity Breit Hamiltonian constant.

8. General non-linear terms in Schrödinger equation

The results obtained so far show without doubt that not only first order terms on the density function can play a role in the definition of non-linear Schrödinger equations but that nothing opposes to consider more general non-linear structures. In order to provide an example of this possibility for both electronic and kinetic density functions, a schematic discussion will be developed.

Supposing that the density functions $\{\rho; \kappa\}$ are known, the following Hamiltonian operator can be used within the extended wavefunction form provided with equation (1):

$$\mathbf{H} = \text{Diag}\left(\mathbf{V} + a(\exp(\alpha\rho) - 1); \frac{1}{2}I + b(\exp(\beta\kappa) - 1)\right),$$

where $\{a; \alpha\}$ and $\{b; \beta\}$ are parameters associated to the non-linear density contributions. The zeroth order Hamiltonian will be the classical one as expressed in equation (10), and the present exponential terms will produce the non-linear contributions in both density

classes. It is easy to see employing a trivial Taylor series expansion on every exponential that the included p th order Hamiltonian non-linear terms could be written in this case:

$$\mathbf{H}_p = \frac{1}{p!} \text{Diag}(a(\alpha\rho)^p; b(\beta\kappa)^p), \quad \forall p \geq 1. \quad (34)$$

The corresponding expectation value can be obtained considering the p th order Hamiltonian term (34) as an isomorphic two-component vector. In this case the following extended density vector can be also defined:

$$|P\rangle = \begin{pmatrix} \rho \\ \kappa \end{pmatrix},$$

so the p th order contribution to the energy expectation value could be simply written as

$$\mathbf{E}_p = \langle P | \mathbf{H}_p \rangle = \frac{1}{p!} (a\alpha^p \langle \rho | \rho^p \rangle + b\beta^p \langle \kappa | \kappa^p \rangle) = \frac{1}{p!} (a\alpha^p \langle \rho^p \rangle + b\beta^p \langle \kappa^p \rangle).$$

A general framework containing non-linear terms in the Schrödinger equation is set in this manner. It must be finally noted that the nature of these p th order correction terms can be associated to $(p + 1)$ th order self-similarity measures involving the two density classes.

9. Conclusions

A significant sample of possible uses of extended Hilbert spaces and the related generalized Sobolev spaces have been studied.

In particular, as a consequence of the broad application scope connected with both extended Sobolev and Hilbert spaces, the non-linear Schrödinger equation has been analyzed, as a mathematical structure issued of particular extended wavefunctions, for simple two-electron cases involving both the closed shell case, as well as the corresponding singlet and triplet monodeterminantal states. A general Slater determinant state function for N -electron systems has been also presented, in the same context employing a technique based on the nested sum operator formalism.

Generalized Sobolev spaces had been finally used to set up the extended wavefunctions and energy expressions for symmetrical non-linear Schrödinger equations, where not only the second power of the wavefunction is present but also two alternative second order terms involving the gradient of the wavefunction. One of them is shown to be the same as to consider the variation of mass with velocity in the Breit Hamiltonian.

The present applications show the methodological capabilities of the extended Hilbert and Sobolev spaces and point the way to easily solve the non-linear Schrödinger equation.

Two points should be, finally, noted. First, from the exposed naive formalism it seems that addition of higher order terms as elements of the extended wavefunction vector could be propitiated by the structure of the extended Sobolev spaces, posing no other problems than those associated to the increasingly difficult structure of the implied

integrals in the corresponding energy expressions. Second, and nonetheless important, this study clearly shows the tight connection of the non-linear Schrödinger equation structure with quantum similarity measures.

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