

Quantum chemistry, Sobolev spaces and SCF

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Extended wavefunctions, including the wavefunction gradient, and the norm induced Sobolev spaces are presented as a mathematical structure well adapted to the approximate quantum-chemical formalism, customarily used to handle the Schrödinger equation. A useful application, related to the solution of SCF Euler equations in matrix form, is also analysed.

KEY WORDS: quantum chemistry, Sobolev spaces, Schrödinger equation, extended wavefunctions, kinetic energy, Sobolev transformation, SCF theory, generalised secular equations, LCAO-MO theory

1. Introduction

Solution of the generalised secular equation, related to the SCF Euler equations in matrix form, can be associated to the pioneering procedure described by Löwdin several years ago [1]. Such generalised secular equations forms appear because of the non-orthogonality problem posed by the use of STO or GTO as AO basis sets within the LCAO-MO formalism [2].

Although other possible transformations of the generalised secular equations, such as the Choleski decomposition [3] or alternative manipulations [4], are possible, Löwdin's transformation has been analysed in deep in the current literature because of the associated implications on MO theory and density function study; see for a recent example the work of Mezey [5].

Löwdin's and the previously quoted alternative manipulations of the generalised secular equation are usually referred to the transformation of the AO basis set *metric matrix*, within the quantum chemical lore customarily also called *overlap matrix*, a term which shall be taken as a synonym of the former mathematical concept. Overlap matrix is, by construction, a positive definite matrix and this property is the basic feature, which is used in all the mentioned procedures. However, within the so-called *ab initio* computational framework, another matrix exists with the same property of positive defi-

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nitiness, namely: the matrix representation of the *kinetic energy* operator. Although the positive definite nature of the kinetic energy expectation value has been used and studied from old times [6–8], as far as we know, there are no literature quotations dealing with the analysis of such a property in the kinetic energy matrix representation, as well as its possible use in practical solutions of SCF Euler equations.

Recently, in our laboratory, an analysis of the structure of the classical quantum-mechanical wavefunction has been carried out [9], and several applications have been published [10,11]. In this analysis the role of the wavefunction gradient has been put forward in such a manner that the gradient components themselves were considered on the same footing as the associated wavefunction, resulting into a new vectorial function formalism, collecting both the wavefunction and its gradient as elements [9]. Several consequences of this procedure have been obtained and employed afterwards.

In a first place, the kinetic energy density can be used to visualise other characteristics of molecular surfaces, which are not contained in the space density alone [9]. Among other possibilities, one can mention the use of kinetic energy density functions in the evaluation of similarity measures [12]. These kinetic energy density similarity measures can be used as molecular descriptors in QSAR equations [13], analogous to the ordinary ones based on space density. A particular application to discuss an apparent MO paradox, related to the existence of nodal planes, has been also published not long ago [14].

Based on previous work, our aim in this paper is to summarise briefly the earlier theoretical results obtained in our laboratory and to associate them to the definition of Sobolev spaces [15]. Once the needed simple mathematical framework is described, an application of these ideas to the transformation of the SCF Euler equations in matrix form will be discussed and a useful new SCF algorithm finally described.

Thus, this paper corresponds to another possible use of the extended wavefunction and total density concepts.

2. Extended wavefunctions

In previous work [9], based on the well-established properties of wavefunctions and their gradients [6–8], an extended wavefunction vector structure was postulated. In order to make easier the following discussion, a résumé of the theory will be initially presented.

2.1. Extended wavefunction and total density function

Suppose known a quantum system state energy–wavefunction pair: $\{\mathcal{E}, \Psi\}$. An *extended* wavefunction can be easily constructed and formally written as the vector

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

Many useful consequences can be deduced from this definition. Among others, the possibility to construct a joint total density involving the usual *electronic* density function:

$$\rho = |\Psi|^2,$$

plus a *kinetic energy* density function:

$$\kappa = |\nabla\Psi|^2,$$

producing a *total* density function:

$$\tau = \text{Tr}(|\Phi\rangle\langle\Phi|) = \rho + \kappa.$$

The fact must be noted now that the total density function is to be interpreted as the probability to find the parent quantum system in either a volume element *or* being associated to a given kinetic energy range. The grammatical particle “or” needs to be stressed and considered as a logical symbol \vee , in order to put in evidence the fact that such composite total density fulfills the uncertainty principle.

2.2. Expectation values within extended wavefunctions

Extended wavefunctions can be used, under the assumption that Schrödinger equation is solved in an approximate manner. In this case, it can be shown that *all* expectation values, even energy-like ones, can be written employing a *statistical* formalism [9]. That is, suppose known a quantum system, then if Ω is taken as an Hermitian operator associated to *any* system observable, and ρ is a system state density function, then the expectation value $\langle\omega\rangle$ of the chosen observable of the system state can be expressed in any case as

$$\langle\omega\rangle = \int_D \Omega\rho \, dV. \quad (2)$$

Implications of this theoretical possibility have been used to study the Hohenberg–Kohn theorem [16], while connecting a generalised form of it with perturbation theory [17].

2.3. Energy and extended wavefunctions

An immediate application of the statistical expectation value integral (2) can be performed in the energy expression of a quantum-mechanical system. If the extended wavefunction (1) is employed and in consequence the system Hamiltonian operator \mathcal{H} (in atomic units) can be rewritten in a diagonal form:

$$\mathcal{H} = \begin{pmatrix} \mathcal{V} & 0 \\ 0 & \frac{1}{2}\mathbf{I} \end{pmatrix},$$

where the potential operator is represented by \mathcal{V} and \mathbf{I} represents a unit operator with the appropriate dimensions to make it compatible with the gradient part of the extended

function. Then, if the expectation value of the Hamiltonian is obtained in the usual quantum-mechanical way:

$$\begin{aligned}\mathcal{E} &= \langle \Phi | \mathcal{H} | \Phi \rangle = \langle \Psi | \mathcal{V} | \Psi \rangle + \frac{1}{2} \langle \nabla \Psi | \nabla \Psi \rangle \\ &= \int_D \mathcal{V} \rho \, dV + \frac{1}{2} \int_D \kappa \, dV = \langle \mathcal{V} \rangle + K,\end{aligned}\quad (3)$$

one can see that not only the energy expression does not change, from the classical sum expression involving both potential plus kinetic energy terms, but also that it can be structured as the sum of two expectation value integrals *statistically* expressed. This result, besides of other fundamental implications, possesses the important consequence to establish a theoretical foundation of the quantum QSAR equations [18].

3. Sobolev spaces and extended wavefunction norm

Sobolev spaces play an important role in mathematical analysis. Defined in 1938 [19], they have also been used in the theory of general relativity [20]. Sobolev spaces [15] are to be considered in general as Hilbert functional spaces [21–23], which can be associated to a Banach space structure [24,25], with the particular characteristic that the norm definition includes the derivatives of the space functional elements. Thus, norms for a function Ψ , belonging to a Sobolev space, can be written as follows:

$$\|\Psi\|_n^m = \sum_{p=0}^m \|\nabla^p(\Psi)\|_n = \sum_{p=0}^m \int_D |\nabla^p(\Psi)|^n \, dV.$$

In the above defined Sobolev norm, the symbol $\nabla^p \equiv \bigotimes_{k=1}^p \nabla$, for $p > 0$, and the convention $\nabla^0(\Psi) \equiv \Psi$ applies. Thus, the Hilbert–Schmidt norm [26] of the extended wavefunction $|\Phi\rangle$, presented above in equation (1), which can be written as

$$\|\Phi\|_2 = \langle \Phi | \Phi \rangle \equiv \|\Psi\|_2^1 = \|\Psi\|_2 + \|\nabla \Psi\|_2,$$

can be considered to induce a Sobolev space structure with Hilbert–Schmidt norms over the wavefunction Ψ , and involving *both* the wavefunction and its gradient.

After having obtained the connection between the total density and Sobolev spaces, one can try to find out some physical interpretation of this abstract situation. Then, using the appropriate definition of Hilbert–Schmidt norm and the usual quantum-mechanical meaning associated to the corresponding integrals, one obtains:

$$\|\Phi\|_2 = \int_D |\Psi|^2 \, dV + \int_D |\nabla \Psi|^2 \, dV = \int_D \rho \, dV + \int_D \kappa \, dV = 1 + 2K,$$

where the normalisation of the wavefunction and the quantum-mechanical definition of the kinetic energy expectation value K have been used; that is,

$$\int_D |\Psi|^2 \, dV = \int_D \rho \, dV = 1$$

and

$$\int_D |\nabla \Psi|^2 dV = - \int_D \Psi^* \nabla^2 \Psi dV = \int_D \kappa dV = 2K, \quad (4)$$

respectively.

Thus, from the extended wavefunction composite density, one can deduce that both space and momentum norms are treated as independent elements of the same structure. This fact inspires the construction of the next section and, in this way, also the development of the main goal of this contribution.

4. Kinetic energy matrix representation and metric matrices

As mentioned above, when the MO-LCAO theory is used to solve the Schrödinger equation in a discrete n -dimensional space framework, the AO basis set not only generates the matrix representations corresponding to the involved operators, but the metric matrix acquires a non-negligible role. In this section, the connection of the kinetic energy matrix representation with the overlap matrix will be analysed.

Thus, in order to start from the well-known principles, let us suppose that an AO basis set is known and that it can be represented by the symbols

$$\langle \chi | = (\chi_1, \chi_2, \dots, \chi_n).$$

Then the overlap matrix \mathbf{S} is defined in terms of the integrals employing in turn the scalar products between pairs of the AO basis set functions:

$$\mathbf{S} = \left\{ S_{ij} = \int_D \chi_i^* \chi_j dV \right\}.$$

On the other hand, the kinetic energy matrix representation \mathbf{K} using the same AO basis set is defined as [27,28]

$$\mathbf{K} = \left\{ K_{ij} = \int_D (\nabla \chi_i)^* (\nabla \chi_j) dV = - \int_D \chi_i^* \nabla^2 \chi_j dV \right\}. \quad (5)$$

Equation (5) has been used from the initial construction of GTO-based integrals [27–29]. In the same manner as equation (4), it is immediately deducible from Green's theorem [30].

By construction, both metric and kinetic energy matrices are positive definite arrays. Such positive definite matrix property has to be joined consequently to the property of being Hermitian with real eigenvalues, which are positive definite too, and thus, those matrices are both non-singular. More information about positive definite matrices can be obtained from [3,31–33].

5. Generalised kinetic energy secular equation and Sobolev transformation

Because of the discussion carried out in the previous sections, a close relationship shall be expected between both \mathbf{S} and \mathbf{K} matrices. It is easy to realise that the *generalised* secular equation of the kinetic energy matrix representation provides one of such connections. Indeed, the following generalised secular equation:

$$\mathbf{KX} = \mathbf{SX}\mathbf{\Delta}, \quad (6)$$

where the eigensystem $\{\mathbf{\Delta}; \mathbf{X}\}$ joins the eigenvalue spectrum collected into a positive definite diagonal matrix $\mathbf{\Delta}$ with the matrix \mathbf{X} , which contains as columns the generalised kinetic energy eigenvectors ordered in the same way as the eigenvalues are.

So far, nothing appears noticeable, but one can focus the attention to the following equalities, which can be straightforwardly deduced. Both equations:

$$\mathbf{X}^+\mathbf{KX} = \mathbf{\Delta} \quad (7)$$

and

$$\mathbf{X}^+\mathbf{SX} = \mathbf{I}, \quad (8)$$

hold at the same time, as a consequence of the fulfillment of the generalised secular equation (6). The symbol $+$ over the matrix \mathbf{X}^+ , present in equations (7) and (8), as well as in the following discussion, stands for the complex conjugation and transposition, applied in arbitrary order over the matrix \mathbf{X} , that is $\mathbf{X}^+ = (\mathbf{X}^*)^T = (\mathbf{X}^T)^*$.

Now one is facing the interesting fact such that the kinetic energy generalised eigenvector matrix \mathbf{X} corresponds to a *non-singular transformation*, which not only diagonalizes the kinetic energy representation matrix \mathbf{K} but also can be *simultaneously* associated to an *orthonormalised* set of column vectors with respect to the metric matrix \mathbf{S} .

So, when dealing with quantum-chemical *ab initio* procedures, such a transformation may be of value when solving generalised secular equations associated to a matrix sum, containing the kinetic energy representation. In these cases, the eigenvector matrix \mathbf{X} can have a leading role as an alternative orthogonalisation transformation of the secular system matrices, corresponding as well as to a simplification of the intervening matrix structure. For obvious reasons, such a transformation will be called from now on a *Sobolev transformation*.

6. Sobolev transformation of SCF Euler matrix equations

A simple but illustrative example of the possible use of Sobolev transformation can be found in the SCF theory in matrix form, first discussed by Roothaan [34] and Hall [35].

When dealing with the closed shell one determinant SCF Euler equations in matrix form, see, for example, the well-structured McWeeny's treatise [2], the following generalised secular equation has to be solved:

$$\mathbf{FC} = \mathbf{SCE}. \quad (9)$$

In the above equation, \mathbf{F} is the Fock matrix, which can be supposedly constructed as the sum of three matrices, in the form [2]

$$\mathbf{F} = \frac{1}{2}\mathbf{K} + \mathbf{N} + \mathbf{R}(\mathbf{C}),$$

where \mathbf{K} is the kinetic energy matrix, \mathbf{N} corresponds to the nuclear attraction operator matrix representation and, finally, $\mathbf{R}(\mathbf{C})$ is the electronic repulsion. The implicit dependence of the repulsion matrix on the eigenvector matrix \mathbf{C} is written explicitly as a functional dependence [34]. The diagonal matrix \mathbf{E} collects the Lagrange multipliers associated to the constrained electronic energy minimisation process [2,34].

The Sobolev transformation can be employed into the generalised secular equation (9). The whole transformation process will yield a new secular equation, which can be written now as

$$\mathbf{F}_S \mathbf{Z} = \mathbf{Z} \mathbf{E},$$

where the Sobolev transform of the Fock operator matrix representation \mathbf{F}_S is easily defined as

$$\mathbf{F}_S = \mathbf{X}^+ \mathbf{F} \mathbf{X} = \frac{1}{2} \mathbf{\Delta} + \mathbf{N}_S + \mathbf{R}_S(\mathbf{C}),$$

while the Sobolev transforms of the nuclear attraction and repulsion matrices are defined in the same way, that is,

$$\mathbf{N}_S = \mathbf{X}^+ \mathbf{N} \mathbf{X}$$

and

$$\mathbf{R}_S(\mathbf{C}) = \mathbf{X}^+ \mathbf{R}(\mathbf{C}) \mathbf{X}.$$

The transformed eigenvectors are related to the initial ones by an inverse Sobolev transform:

$$\mathbf{Z} = \mathbf{X}^{-1} \mathbf{C}. \quad (10)$$

However, the inverse of the eigenvector Sobolev transform \mathbf{X} will be usually never needed in the present SCF algorithm. This is so because, once the Sobolev transformed Fock operator matrix \mathbf{F}_S is known, and its eigenvectors \mathbf{Z} are computed by means of any standard diagonalization procedure [3], then the original generalised eigenvectors \mathbf{C} can be simply retrieved by the immediate product of the Sobolev transform matrix, in such a way as

$$\mathbf{C} = \mathbf{X} \mathbf{Z}.$$

So, in this manner a sketch of the procedure, which one must follow when using Sobolev transformation in SCF algorithms, has been established.

In appendix a simple way to compute the Sobolev transform inverse, as appearing in equation (10), is presented along with other properties of interest.

7. Sobolev transform in SCF algorithm

From the discussion above performed, one can construct straightforwardly the following scheme, whose steps schematise the procedure to be carried out, if Sobolev transformation is to be used in solving such a SCF problem. For simplicity, a closed shell monodeterminantal computation has been chosen. The SCF algorithm described by Veillard [36] can be consulted for details referring to the fundamental aspects other than Sobolev transformation.

SCF and Sobolev transform algorithm

- (A) Compute \mathbf{S} , \mathbf{K} matrices.
- (B) Solve the generalised secular equation $\mathbf{KX} = \mathbf{SX}\mathbf{\Delta}$.
- (C) Compute \mathbf{N} and Sobolev transform it: $\mathbf{N}_S = \mathbf{X}^+\mathbf{N}\mathbf{X}$.
- (D) Compute the repulsion hypermatrix \mathbf{G} .
- (E) Compute the Sobolev-transformed one-electron Hamiltonian: $\mathbf{h}_S = (1/2)\mathbf{\Delta} + \mathbf{N}_S$.
- (F) Set initial Sobolev-transformed Fock operator: $\mathbf{F}_S \leftarrow \mathbf{h}_S$.

SCF: *do*

- (a) Solve the secular equation $\mathbf{F}_S\mathbf{Z} = \mathbf{Z}\mathbf{E}$.
- (b) Retrieve MO eigenvector matrix $\mathbf{C} = \mathbf{X}\mathbf{Z}$.
- (c) Compute charge and bond order matrix $\mathbf{D} = 2 \sum_{k \in \mathcal{C}} \mathbf{c}_k \mathbf{c}_k^+$.
- (d) Perform convergence tests: if converged, *exit* SCF.
- (e) Compute repulsion matrix by the contracted product: $\mathbf{R}(\mathbf{C}) = \mathbf{G} : \mathbf{D}$.
- (f) Sobolev transform the repulsion matrix: $\mathbf{R}_S(\mathbf{C}) = \mathbf{X}^+\mathbf{R}(\mathbf{C})\mathbf{X}$.
- (g) Construct a new Sobolev-transformed Fock operator: $\mathbf{F}_S \leftarrow \mathbf{h}_S + \mathbf{R}_S(\mathbf{C})$.

End do SCF.

End of the algorithm.

Several tests of Sobolev algorithm as above described have been made within SCF programs entirely developed in our laboratory. The results, obtained in a wide variety

of closed shell molecular systems and basis sets, show, in a first instance, the same behaviour as classical SCF procedures.

On the other hand, it is not so difficult to imagine that similar steps and algorithms can be devised for other SCF forms, mainly in open shell structures as defined by one of us several years ago [37–39].

At the same time, the Sobolev transformation not only can be viewed as a possible alternative transformation of the Fock matrix for SCF purposes, producing a neat diagonalization sequence and an elegant algorithm. On the contrary, Sobolev transformation can be also considered as a global AO integral transformation which can prepare the computational problem in such a way as to yield an orthonormalised non-local basis set, leaving the system's energy invariant and possessing appealing properties for further applications.

8. Conclusions and final remarks

8.1. Conclusions

The most interesting result of this paper may be associated to the fact that, through Sobolev spaces, it is clearly shown that the extended wavefunctions, constructed containing both the wavefunction itself and its first derivative, acquire a well-defined Banach space structure. In consequence: a sound Hilbert space form.

One can also admit that within LCAO-MO theory, in a way suggested by the Sobolev space structure of the deducible extended density function, the metric and kinetic energy representation matrices are easily connected in terms leading to a useful transformation matrix.

Sobolev spaces and the derived transformation, involving the generalised eigenvectors of the kinetic energy matrix representation, can be considered as an appreciable mathematical tool, which can turn to be of value in the computational world of quantum chemistry, and more specifically, in the discrete matrix representation scenario of the involved Hermitian operators associated to system observables.

A straightforward application procedure, designed in order to simplify the SCF algorithm, can be easily built up from the theory of Sobolev wavefunction extended spaces.

8.2. Remarks

Extension of the quantum-chemical Sobolev norms to higher derivatives will naturally lead first to the introduction of a mass variation with velocity term [40], which has already been employed to visualise alternative molecular density surfaces [9]. Thus, a term appearing in Breit Hamiltonian [41] will follow. This will induce the presence of the wavefunction Laplacian in the extended wavefunction structure and, consequently, the Laplacian norm in the corresponding Sobolev space. This possibility points out towards the connection between classical and relativistic formulations of quantum chemistry. A first attempt in order to elucidate this connection has already been made [9].

The possibility to add more terms in the extended wavefunction vector seems appealing. This may be used to obtain non-linear or alternative Schrödinger equations other than equation (3), see for an excellent review the work of Fraga et al. [42]. Such procedures will lead into extended Sobolev spaces, as well as other alternatives and structures still waiting to be disclosed.

However, these appealing possibilities will not be further discussed here. The reason to proceed like this can be justified in order to preserve as much as possible the plainness and the beauty of the simplest Sobolev space features, when applied to one of the most usual quantum-chemical problems.

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Appendix. Sobolev transform inverse

From inspection of equation (8), it appears immediately that the inverse structure \mathbf{X}^{-1} of the Sobolev transformation \mathbf{X} can be written as the trivial matrix product:

$$\mathbf{X}^{-1} = \mathbf{X}^+\mathbf{S}. \quad (\text{A.1})$$

This result may appear at first glance as an inverse on the left, but taking into account that the following matrix product,

$$\mathbf{P} = \mathbf{X}\mathbf{X}^+\mathbf{S},$$

can be considered as a projector over the *full* space generated by the kinetic energy generalized eigenvectors, then also it can be equivalently written:

$$\mathbf{X}\mathbf{X}^+\mathbf{S} = \mathbf{I}.$$

In this way, one can consider that equation (A.1) corresponds to a full inverse of the Sobolev transform. Consequently, equation (10) can be written alternatively as

$$\mathbf{Z} = \mathbf{X}^+\mathbf{S}\mathbf{C}.$$

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