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Fundamental relationships between elementary functionals in quantum chemistry. An application for H_2 and H_2^+

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ABSTRACT

General sets of differential equations have been formulated on the basis sets completeness of the Hilbert space when using operators of the molecular Hamiltonian. In these equations, different relationships between elementary functionals (EF) have been found depending of functions of the overlap, and overlap derivative. Applications of these relationships to simple systems (example: a diatomic molecule with two basis components) were performed. Similarities of early approximations for parametric quantum methods were obtained. The molecular total energy for H_2 and H_2^+ using minimal basis set was found to be as a function of the overlap plus two integration constants. This way, it may be calculated in terms of dissociation energy and equilibrium bond distance of the molecules. Selected trial overlap, as an exponential function, consistently gives values above the exact potential energy curve (PEC) for the ground state. The optimized overlap exponent at each internuclear distance gives better PECs with respect to minimal basis sets. Results suggest an optimal overlap associated to a complete correlated minimal basis set. In particular, a *q*-exponential function as a model of the overlap gives energy values to a very near exact PEC.

1. Introduction

The structure of quantum mechanics (QM) is based on functional analysis and the application of minimax principle (MMP) [1,2]. Therefore, exploring new relationships between EFs may be relevant in the development of novel methods for the evaluation of electronic properties of materials. In this sense, chemistry is the area of science dealing with bond breaking and bond formation between atoms, synthesis, material transformations, and molecular spectra. A branch of this area is quantum chemistry (QC) where applications of mathematical methods to QM are used for modeling chemical processes. At present, a fast increase of QC utilization in experimental chemical research is very popular, because appears to complement experimental works, interpretation of results, and exploration and discovery of new chemicals and materials.

A great variety of modifications to QC methods have been carried out, in the last decades, in order to be more efficient and accurate. Also, they have been designated by the way of EFs (integrals) evaluation. Three different types of methods are used: (a) parametric or semiempirical (all EFs depend on parameters), (b) Density Functional Theory (DFT), i.e., EFs are functionals of density and depend on some parameters, and (c) *ab initio*, all EFs are analytically calculated using optimized parameterized basis sets. For the last methods, explicit wave functions are defined in different manners from finite selected basis sets of the Hilbert space.

Each method requires a set of differential equations for solution when applying several approximations. If approximations are strong, the results may be of qualitative information, yet, they are widely used for pragmatic reasons because of its simplicity and low computational cost. On the other hand, accurate methods [3] are expensive and complicated to be routinely applied. Thus, a balance between accuracy and computational expenses is convenient for practical purposes. In this sense, modeling of industrial and technological materials requires approximate methods, because of the complexity and size of chemical systems. Consequently, the improvement of more efficient and operative QC tools is of significant importance due to the manifold applications in developing new materials for modern technologies. Alternative methods may be formulated not in terms of basis sets, but based on parameters (parametric or semiempirical methods). Thus, the wave-function space is unknown and the Hamiltonian expectation value is defined in terms of parametric functionals for which the basis set is implicitly included [4].

Recently, several improvements have been proposed for parametric quantum methods (PQM) [5–14], considering different applications for specific purposes. Nevertheless, parametric EFs

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(PEF) have not been connected to fundamental principles of QC. For example, changes of basis set elements $\{\phi\}$ producing variation of PEFs which has to be related with other PEF variations. Since, basis sets are intrinsically included into PEF, there is not guaranty that each PEF comes from the corresponding elements of the basis set. Consequently, misleading results may appear, due to a loss of balance between different energy functional components that give the correct convex behavior of the PEC.

In previous work [15], fundamental issues of PQM methods such as sets of elementary functionals (SEF) and MMP were discussed. This publication [15], a comparison between analytical and PEF based on q-exponential functions for H-H, C-C and C-H pairs of atoms were performed. A reasonable modeling of H^{core}, electron-nucleus potential, overlap, and Coulomb two-electron integrals were obtained. Nevertheless, no correlations between PEFs parameters were reported. Consideration about the relationships between SEFs may be relevant, because it would be possible to reduce the number of EFs in QC methods.

An active field of research is to find an efficient algorithm to evaluate and to reduce the number of EFs or integrals [16–20]. Optimal transformed minimal basis set (OTMBS) [4,16] or chemically deformed and oriented atomic minimal basis set orbitals [17–20] have been used. In the case of PQMs, EF simulation is performed by adjusting them to simple parametric functions that depend on the inter-atomic distances and parameters. Yet, standard PQMs use different types of PEFs, as mentioned above, absence of any relationship between them. The present work may establish, in general, EF relationships in terms of the overlap and its derivative. The importance of these relationships is not only relevant for PQMs but for all types of QC methods. Many efforts have been dedicated in the past years to improved techniques for efficient evaluation of two-electron-integrals [21–23]; and also to find schemes in order to avoid their calculations. In this sense, these relationships can be employed as an alternative to evaluate two-electron repulsion integrals that still present an obstacle for all QC techniques.

The present work is organized in the following way: (a) A theoretical background about EF for one and two electrons is presented in Section 2. (b) General relationships between EFs considering the variation of the corresponding functional with respect to a parameter; e.g. the internuclear distance, are displayed in Section 3. (c) A description of this theory for the simplest diatomic molecules (H_2 and H_2^+) using minimal basis sets in terms of submatrices is given in Section 4. (d) Applications to H_2 and H_2^+ are exposed to calculate PECs in Section 5. (e) Finally, conclusions and comment for further work are described in Section 6.

2. Theoretical background

Electronic energy calculations in QC for molecular systems are results from solution of the time-independent Schrödinger equation (TISE),

$$\widehat{H}|\Psi_I\rangle = E_I|\Psi_I\rangle, \tag{1}$$

where $\widehat{H}$ is the electronic Hamiltonian operator, and $|\Psi_I\rangle$ corresponds to the multi-electronic wavefunction for the state I of a molecular system of n electrons and N nuclei. This wavefunction belongs to the Hilbert space $\mathcal{H}$ in R^{3n} and it is expanded in terms of a complete basis set $\{\phi_\mu\}$, where each ϕ_μ has a domain in R^3.

2.1. Operators and functionals

The E_I variable corresponds to the eigenvalue of state I. $\widehat{H}$ normally is approximated to a non-relativistic Born-Oppenheimer (NRBO) molecular operator of the TISE. An expression of this operator, given in a compact way, is the sum of one-electron ($\widehat{H}^{core}$) and two-electrons ($\widehat{G}$) operators,

$$\widehat{H} = \sum_{i=1}^{n}\widehat{H}_i^{Core} + \sum_{i=1}^{n}\sum_{j\geqslant i}^{n}\widehat{G}_{ij.} \tag{2}$$

The first term in Eq. (2) (one-electron operators, core-Hamiltonian ($\widehat{H}_i^{Core}$) is expressed as a sum of kinetic ($\widehat{T}_i$)and potential energy ($\widehat{V}_{iA}$) operators,

$$\widehat{H}_i^{Core} = \widehat{T}_i + \sum_{A=1}^{N}\widehat{V}_{iA} = -\nabla_i^2 - \sum_{A=1}^{N}\frac{Z_A}{r_{iA}}. \tag{3}$$

where $r_{iA} = |\vec{r}_i - \vec{R}_A|$ is the distance of electron i to nuclei A, and Z_A is the nuclear charge of atom A.

The two-electron operators represent electron-electron repulsion interactions,

$$\widehat{G}_{ij} = \frac{1}{r_{ij}}, \tag{4}$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ corresponds to the distance between electrons i and j.

As a matter of simplicity, we began our study using the closed shell and one single Slater determinant wavefunction (Hartree-Fock-Roothaan (HFR) or Kohn-Sham (KS)). In this context, all types of EF were used in all methods for NRBO molecular operator of the SE. The electronic energy expression (E_0) of HFR for the ground state, considering a number of K basis set, is given as,

$$E_0 = \frac{1}{2}\sum_{\mu}^{K}\sum_{\nu}^{K}P_{\nu\mu}\left(H_{\mu\nu}^{Core} + F_{\mu\nu}\right) \tag{5}$$

where

$$H_{\mu\nu}^{Core} = T_{\mu\nu} + \sum_{A}^{N}V_{\mu\nu}^{A}, F_{\mu\nu} = H_{\mu\nu}^{Core} + \sum_{\lambda\sigma}^{K}P_{\lambda\sigma}\left[G_{\mu\nu\sigma\lambda} - \frac{1}{2}G_{\mu\lambda\sigma\nu}\right] \tag{6}$$

$T_{\mu\nu}$, $V_{\mu\nu}^{A}$,and $G_{\mu\nu\sigma\lambda}$, are kinetic, potential energy, and two-electron elementary functionals. The term $P_{\lambda\sigma} = 2\sum_a^{n/2}C_{\lambda a}C_{\sigma a}^{*}$ is the electronic density matrix and the sum ranges over the occupied orbitals, where $C_{\lambda a}$ are coefficients of the molecular orbitals expansions. In general, matrix C is calculated using a self-consistent-field (SCF) procedure, when considering in some cases symmetric properties of the molecular geometry.

2.2. Optimal minimal basis sets

The employment of correlated orbital [24,25] has demonstrated, in practice, that it is possible to introduce part of electronic correlation into the energy expectation value using a single determinant wavefunction as trial functions. In parametric methods, correlation functions for multicenter interactions are assumed to be included through SEFs that depend on the internuclear distance of the considered orbitals. These functionals implicitly describe correlation as an average for each type of interatomic interaction. In the case of intra-atomic correlations, they are included in parameterization of repulsive and attractive electronic interactions with respect to different atomic excitations that correspond to different occupied orbitals. A molecular orbital (χ_i) in Hartree-Fock or DFT approaches may be expressed as,

$$\chi_i(\{\vec{r}\},\{\vec{R}_A\}) = \sum_{A}^{N}\sum_{j_A}^{n_{KA}}c_{j_A}^{i}\varphi_{j_A}(\vec{r},\vec{R}_A) \tag{7}$$

where N is the number of atoms, n_{KA} the number of basis set of atom A, and each element of the atomic basis is, in principle, defined by,