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REGULAR ARTICLE

From Hartree–Fock and Heitler–London to chemical orbitals

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Abstract For chemistry the theoretical representation of the forces connecting atoms in molecules was and is a central problem. The Atomic Orbital and the Molecular Orbital are basic building blocks in the Heitler–London (HL) and in the Linear Combination of Atomic Orbitals–Molecular Orbital (LCAO-MO) methods, which have lead to the construction of modern Valence Bond and Hartree–Fock methods (and related extensions). However, accurate predictions from non semi-empirical methods often require enormous amount of computer power, if applied to molecules of reasonable size and current chemical interest. We have critically re-examined the two basic methods and suggested a few extensions. Merging of the Hartree–Fock with the Heitler–London algorithms, as recently proposed in the Hartree–Fock–Heitler–London (HF–HL) method, reduces the length of the expansions needed in AO or MO ab initio models in the computation of binding energy; this simplification allows easy interpretation of the resulting wave function. The HF–HL method is exemplified with systematic computations on ground and excited state of the hydrides and homonuclear diatomic molecules with atoms of the first and second period of the periodic table. Further, we show that the HF–HL method is derivable from a wave function constructed with a new type of orbital, the Chemical orbital (CO), which embodies the characterization of MO near equilibrium, AO at dissociation and at the united atom. Preliminary computations with CO are included. The new method provides the conceptual origin of both the HF and VB approaches, thus the foundation of an 80 years effort in variational quantum chemistry.

Keywords Atomic · Molecular · Chemical orbitals · Hartree–Fock · Heitler–London · Hartree–Fock–Heitler–London · Diatomic hydrides · Diatomic homopolar molecules

1 Introduction

In this work, we consider models proposed to represent the chemical bond. However, to define a chemical bond we need a number of concepts, particularly those of “molecule”, “atom”, “electron”, and “nucleus”. These concepts have slowly evolved in the last two millennia. For the evolution of chemical models in the Western world, describing chemical theories from Greece classical time to 1914, the year of the Bohr atom, we refer to a recent study [1], to the encyclopedic work by Geymonat [2] and to the volume by Bensaude-Vincent and Stengers [3].

We follow in some detail the evolution of the atomic and molecular orbital models by presenting representative sets of computations on simple diatomic molecules with the traditional Hartree–Fock (HF) and Heitler–London (HL) models. Further, we expose the Hartree–Fock–Heitler–London model (HF-HL) recently proposed and tested. The computational examples for this model are diatomic hydrides, HX, and homopolar molecules, X_2, with X the atoms of the first and second period of the atomic table. Analyses of the HF–HL model leads to propose a

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new one-electron function, designated Chemical Orbital (CO), tested for the H_2 and LiH ground state molecules.

In this section, we outline the presentation of our work. In Sect. 2, we briefly recall the emergence of quantum mechanics and its early impact on chemical models.

In Sect. 3, we introduce the atomic and the molecular orbitals, AO and MO, the one-electron function concepts proposed in the "fantastic few years" when Slater [4] introduced the determinantal form to represent the electronic wave function, Born and Oppenheimer [5] assumed the near-independence of electronic and nuclear motions, Hund [6] and Mulliken [7] proposed linear combination of Atomic orbital, the LCAO-MO model, and Heitler and London presented what today is called the Heitler–London model [8].

Since those early days two different models, LCAO–MO and HL, have been widely used, based one on MOs the second on AOs, the "bricks" to construct the zero order molecular wave functions, as explained by Herzberg [9] in his classical volume. The two methods yield solutions which differ from the exact non-relativistic solution by an amount called by Wigner [10] "correlation energy", E_c; this correction can be obtained as electronic density functionals [11–16], the main task of Sect. 3. The use of density functional to correct the HF energies was essentially ignored in the period 1930s–1980s, with few exceptions [11–16]. To cope with the correlation error the HL model evolved into the several Valence Bond (VB) variants [17–23]; likewise the LCAO-MO (in the improved form of molecular Hartree–Fock (HF) [24–28]) evolved into the Multi-Configurations (MC) [29–36] and Configuration interaction (CI) [37, 38] expansion techniques (generally very long linear combinations of determinants).

In Sect. 4, we report and compare HF and HL computations, using the same basis sets, on hydrides and homopolar diatomic molecules, needed in the following of the paper.

In Sect. 5, we discuss the near degeneracy of configurations in HF and HL solutions, presenting various decompositions of the correlation energy correction, a basic aspect in the HF–HL strategy.

In Sect. 6, we present the HF–HL model [39–44]. In Sect. 7, we exemplify the HF–HL model by computing binding energies [42, 43] for the diatomic molecules previous analyzed with the HF and HL models, using basis sets of the same type as those used in Sect. 4.

In Sect. 8, we account for part of the atomic correlation neglected in Sect. 7; for this task we use mainly the Coulomb hole density functional approximation (DFA) [41] summarized in Sect. 3.

In Sect. 9, we show that the HF–HL model can easily and correctly predict excited state transitions.

In Sect. 10, we show that the HF–HL model is an approximation of a more general model, the Chemical orbitals wave function, Ψ_{CO}, constructed with a new, compact and easily interpretable one-electron function [44], the CO. Applications of the Chemical orbital method to the H_2 and LiH ground states are reported in Sects. 11 and 12, respectively.

Section 13 attempts to trace the genealogy of the HF–HL method and of the CO representation from selected approximations in computational chemistry. In Sect. 14, we present a conclusion.

In modern computational quantum chemistry two goals are essential: first, quantitative accuracy and, second, physical interpretability to allow reliably transferability of computational predictions from molecule to molecule, a step aiming to a "quantitative theory for properties transferability". By now computational chemistry has become another "laboratory" technique, based on complex manipulation of numerical data via computer codes often commercially available. Thanks to the progress in computer technology, particularly parallel computers [45], the HF-based models (CI and MC) have essentially reached the goal of quantitative accurate predictions [34, 36] for small molecules, and the different VB models [23] have made notable progress towards physical interpretability. In the mean time perturbation approaches have also made most notable strides [46–48], but again with the "sine qua non" condition of ample computational facilities. Recently, Quantum Monte Carlo (QMC) computations offer a most evident example of numerical techniques fully dependent on availability of very ample computer power [49, 50]. To lessen the extreme computational demand of ab initio methods, semi-empirical methods were used in the past [51] as well today [52–54], particularly in applied computational chemistry; this trend constitutes another indication of the need for some novel approach for the prediction of bond energies.

For reviews on the present status and developments of quantum chemistry we refer to two recent volumes [55, 56] and to a recent special issue in the *Journal of Computational Chemistry* [23]. For a review on progress of parallel computer technology we refer to a special issue in Parallel computing [45].

2 Early quantum theory in chemistry

The discovery of the electron by Thomson (1897) and the subsequent need of a new mechanics shuttered the simplicity of nineteenth century chemistry [1–3]. The classical continuous energy distribution idea was contested by Plank [57], the classical space–time frame was replaced with new spaces by Hilbert [58] and Einstein [59]. Nothing was left unchallenged as a consequence of de Broglie [60] wave mechanics, of the electron spin discovery by Uhlenbeck and Goudsmit [61], of the Pauli principle [62], of the 1926

Schrödinger equation [63], of the Fermi [64] and Thomas [65] simple electronic density formulation of the atomic energy, and of Dirac relativistic formulation [66]. New concepts were introduced like uncertainty, wave functions, orbitals and spinors, probability density, multiplicity of states, couplings in the motion of electrons and spins, etc.

Initially, following the introduction of Bohr's model [67], chemist's intuition did provide a bridge linking chemical structures to the finding of the new atomic physic. Thus Lewis [68] assumed that two electrons, one from one atom and the second from another atom, "the electron-pair", form the chemical bond between atoms in molecules (a rather unorthodox view, since from the Coulomb law two electrons repel each other). The Lewis pair nicely provided an apparent justification to recently obtained chemical structure formulas for most single and multiple molecular bonds; the model theoretical foundations were strengthened with the discovery of the electron spin, by assuming anti-parallel spins for the electron pair.

However, the never ending desire for self-consistency in different fields of science did lead to the need to understand the "formation" and "breaking" of "chemical bonds" via a direct utilization and solution of the quantum mechanical laws, particularly the Schrödinger and Dirac equations. This implies the need to solve with quantum mechanical models the equations of motion for the atoms and electrons in molecules, and as a by-product to determine the stability (or instability) of certain geometrical configurations between the atoms in a molecule. The belief of an "affinity" between atoms in a molecule [1–3] is thus replaced with a quantum mechanical understanding of the dynamics of the electrons in the atoms constituting a molecule.

The electronic structure of atoms, clearly, were the first target. In 1928, Fermi [64] and Thomas [65] proposed a simple electronic density model based on the Poisson equation to approximate the electronic atomic structure. The model was improved by Hartree with a product of one electron functions [69], later extended by Hartree [70, 71], Slater [4] and Fock [25] with the determinantal wavefunction, yielding the Hartree–Fock model. Shortly thereafter Möller and Plesset [46] used a perturbation approach. Finally, Dirac [66] proposed a general Hamiltonian including relativistic effects. The correlation energy error associated to the Hartree–Fock model was considered by Hartree et al. [29] for near-degenerate states, by Hylleraas with an explicit r_{ij} dependency in the wave function [72], by the CI algorithms [37], and with a density functional by Wigner [10]: a long series of investigations which continue today.

The impact on molecular theory was nearly simultaneous to the berth of wave mechanics, thanks to well-recognized pioneers, particularly E. Schrödinger (1887–1961), F. Heitler (1904–1981), F. London (1900–1954), L. Pauling (1901–1994), F. Hund (1896–1997), J. C. Slater (1900–1976), R. S. Mulliken (1896–1986), G. Herzberg (1904–1999), D. Hartree (1897–1958), W. Pauli (1900–1958), P. M. Dirac (1902–1984), V. A. Fock (1898–1974), L. H. Thomas (1903–1992), E. Fermi (1901–1954), E. Wigner (1902–1995) and others. In the period 1928 to 1935, these pioneers proposed the first road map for a quantum theory of the electronic structure of many electron molecules, but numerical solutions had to wait for the electronic industry, emerged shortly after the end of the second world war.

3 Atomic and molecular orbitals and the Coulomb hole functional

It is well known that, at the beginning of quantum chemistry in the early 1930s, two approaches were predominant in the attempt to explain, with quantum theory, the forces responsible for holding atoms in a molecule. These were the Linear combination of atomic orbitals–molecular orbitals [6, 7] (LCAO–MO), and the Heitler–London [8], HL, approximations, resulting from two different concepts embodied in the MO and AO one-particle functions, respectively.

Quoting Herzberg [9], the building-up principle to construct molecular wave functions rests on the observation that "the number of electronic states in a molecule is of the same order as for atoms". Further, we recall that the manifold of electronic states in a molecule can be obtained, as for atoms, by successive bringing together of the parts (building-up principle). The molecule can be built up starting at dissociation by bringing together the whole atoms of which it consists (HL and VB approaches); alternatively, we may split the united atom (HF approach). Finally, the individual electrons are added one after the other to the nuclei, which are assumed fixed, considering in which orbitals the electrons will arrange themselves. This leads to Herzberg [9] and Mulliken [73] orbital correlation diagrams, which make use of both AO and MO one-electron functions to describe the electronic distribution from infinite separation to the united atom, subject to the symmetry and spin constrains expressed by the Wigner and Witmer rules [74].

We should point out, however, that in general neither the HL nor the HF models did fully follow the suggestion contained in the correlation diagrams, namely a one-electron function obtained by considering both the AO and the MO type functions, thus valid from dissociation to the united atom; in Sect. 11, we return on this forgotten point.

An obvious fault of the HF method is the assumption that the same orbital function can be used to describe the distribution for two electrons, an assumption which reveals all its inconsistency at dissociation; for the HL method this problem does not exist since it dissociates correctly. A second obvious fault, shared by both methods, HF and HL, is the assumption that two interacting electrons approaching zero inter-electronic distance can be placed "one on top of the other". Since the early days of quantum chemistry Hylleraas made clear that this assumption is unphysical; unfortunately Hylleraas correction algorithm [72] was (and partly is) rather unpractical. Since the HF method allows two electrons with anti-parallel spins to come too near one to the other, the resulting HF repulsion is too large, thus the total energy is too small by an amount called by Wigner [10] "correlation energy".

Wigner introduced the idea that around each electron there is a shield [10] which prevents another electron to get too close. The shield is stronger for electrons with parallel spins, since not only the electric charges repel each other, but there is also the anti-symmetry of the HF function (Pauli principle). For two electrons with opposite spin the electric charges repulsion is mitigated by spin compatibility. Since the shield opposes the electron–electron approach, its effect is an energy stabilization, thus it corresponds to an energy hole. The shielding for electrons with parallel spins is called Fermi hole (the exchange energy), from anti-parallel spins Coulomb Hole. Wigner [10] estimated the correlation energy correction by fitting the free electron model correlation energy with a functional of the electronic density. Wigner considered the Coulomb Hole correlation energy as a correction to be estimated once a density, ρ_{m}, was available from some model, for example the HF model. This view was followed and extended particularly in pre Second World War Europe as documented in Gombas volumes [11, 12] and papers [13, 14]. The general form of Wigner density functional is

$$E_{\mathrm{c}} = \int \rho_{\mathrm{m}} \varepsilon_{\mathrm{c}}(\rho_{\mathrm{m}}) \mathrm{d}\tau \tag{1}$$

where ρ_{m} is the electronic density from a model m, and the functional $\varepsilon_{\mathrm{c}}(\rho_{\mathrm{m}})$ is [11, 13] of the form:

$$\varepsilon_{\mathrm{c}}(\rho_{\mathrm{m}}) = \frac{a_1 \rho_{\mathrm{m}}^{1/3}}{\left(a_2 + \rho_{\mathrm{m}}^{1/3}\right)} + b_1 \ln\left(1 + b_2 \rho_{\mathrm{m}}^{1/3}\right) \tag{2}$$

with a_1, a_2, b_1, and b_2 fitting numerical parameters from the electron gas. This expression is particularly well suited also for the computation of a fraction of the HF correlation energy, namely for partially correlated wave functions, requiring, however, a re-optimization of the parameters [15, 16, 75, 76].

Since the early 1950s Slater at MIT was interested in efficient computations of the exchange integrals in solid state computations [77] and this did lead to the Hartree–Fock–Slater wave functions (HFS), a very reasonable approximation to the Hartree–Fock functions; the HFS was systematically applied to ground state atomic functions by Hermann and Skillman [78] in 1963. We recall that the status of quantum chemistry from the early days till 1960 is well represented by the special report on the Boulder, Colorado, International Conference in 1959 [79].

In the early 1960 Clementi at IBM published a series of papers with hundreds of RHF wave functions for atoms and ions [80–83] and molecules, thus demonstrating that the Roothaan Restricted–Hartree–Fock method could be systematically adopted in quantum chemistry. The atomic compilation was eventually condensed into "Atomic Tables" [84] and later into the "Roothaan–Hartree–Fock Atomic Wave Functions" [85] tabulation, for neutral, positive and negative ions from He to Xe, using minimal, double zeta and extended Slater-type basis sets. The study with different basis sets was performed to help the progress of molecular computation, since it was assumed that the many center integrals with Slater functions would be eventually routinely available. The tabulation did lead also to the first systematic tabulation of atomic correlation energies [86–89] and to perturbation computations of the relativistic correction [90, 91]. At the same time computations on small molecules and even of molecular interactions (the so called super-molecular approach) were vigorously pursued. Computational chemistry had started!

Clementi's early correlation energy estimates were obtained by subtracting the HF energy from the experimental energy and correcting for relativistic effects [90, 91]. A different approach was also implemented, namely a computational estimate of the correlation energy with a semi-empirical density functional.

As we all know, the relations between the exact non relativistic energy and the HF energy are given (considering for simplicity closed shell structures) by

$$E_{\mathrm{HF}} = \sum_i h_i + \sum_i \sum_j \left(2J_{ij} - K_{ij}\right) \tag{3}$$

and

$$E_{\mathrm{exact}} = \sum_i h_i + \sum_i \sum_j \left(2J_{ij} - K_{ij}\right) + E_{\mathrm{C}} \tag{4}$$

with both equations obeying the virial theorem. E_{c}, a relatively small perturbation, can be represented as a term by term correction, Δ, of the HF energy components; therefore we can write the correlation energy as

$$E_{\mathrm{C}} = \sum_i \Delta h_i + \sum_i \sum_j \left(2\Delta J_{ij} - \Delta K_{ij}\right) \tag{5}$$

and

$$E_{\text{exact}} = \sum_i h_i^* + \sum_i \sum_j \left(2J_{ij}^* - K_{ij}^*\right) \tag{4b}$$

with $h_i^* = h_i + \Delta h_i$, $J_{ij}^* = J_{ji} + \Delta J_{ji}$ and $K_{ij}^* = K_{ij} + \Delta K_{ij}$ the correlation corrected energy components. Thus, we have reached the conclusion that the exact electronic energy essentially retains the structure of the HF energy expression and, therefore one simply needs a correction in the HF algorithm. Physically, since the Coulomb term is overestimated in the HF model, there is the need of a correction which—in a self consistent approach—will bring about corrections primarily in the exchange but also in the one electron terms.

To decrease the HF Coulomb energy in the HF–SCF computation one can simply screen the two interacting electrons, for example replacing $1/r_{12}$ with $1/(\varepsilon r_{12})$, where ε is a screening parameter. Wigner's idea of a radius $r(i)$ for electron i with spin up, delimiting a space region impermeable to electron j with spin down, suggest a Coulomb hole functional [92] to replace the standard Coulomb matrix elements between electrons i and j. In the computation of the Coulomb integrals, the integration from 0 to infinity over the radial coordinates $r(i)$ of electron i and the integration over the radial coordinates of $r(j)$ for electron j is modified at $r(i) = r(j)$, where the two electrons are sharply kept apart in an interval from $r_a = (r(i) - \delta/2)$ to $r_b = (r(i) + \delta/2)$, where δ is a interval value (distance) given from a semi-empirical parameter density dependent [92]. Thus the standard Coulomb interaction matrix element

$$\int_0^\infty f(i)\left[\int_0^{r(i)} f'(j)\mathrm{d}r(j) + \int_{r(i)}^\infty f''(j)\mathrm{d}r(j)\right]\mathrm{d}r(i) \tag{6a}$$

is replaced by

$$\int_0^\infty f(i)\left[\int_0^{r_a} f'(j)\mathrm{d}r(j) + \int_{r_b}^\infty f''(j)\mathrm{d}r(j)\right]\mathrm{d}r(i) \tag{6b}$$

where $f(i)$, $f'(j)$, $f''(j)$ are the standard Coulomb integral expressions relating the orbital basis set representation for electrons i and j, respectively [93]. Note that the above integration over the radial part of the basis set functions was performed after the integration over the angular part, thus δ was parameterized for specific combinations of s, p, d, f, …, etc. functions. The above cut off is "hard", thus the expression in Eq. 6b is designated as the "hard Coulomb hole". Later the original "hard Coulomb hole" was modified into "a soft Coulomb hole" [94] by replacing the Coulomb operator $[1/r_{ij}]$ with the operator

$$\left[1 - \exp\left(-\alpha r_{ij}^2\right)\right]/r_{ij} \tag{7}$$

The value of α, a semi-empirical density dependent value, was determined by fitting atomic energies and ionization potentials for specific combinations of s, p, d, f, …, etc. atomic functions.

The idea to introduce correlation via modifications of the HF interactions, e.g. with the Coulomb hole [92, 94] or with Wigner-type density functionals [10–16, 75, 76], was preceded by the Slater's proposal to extend the role of the HF exchange energy [93]. Clearly the exact non-relativistic energy can be obtained by modification in the HF algorithm either by decreasing the Coulomb energy (Coulomb hole approach) or by increasing the Exchange energy; Slater work eventually leads to the "$x\alpha$" approximation [95]. Thus DFA, are recurring ideas from mid-1930s to mid-1960s based on the assumption of availability of an HF type function, which can be easily corrected; computational chemist attention, however, in the 1960s and 1970s, was predominately focused on linear expansions, either CI or MC–SCF and perturbation methods.

From the 1960 to the 1990 the expression in Eq. 4b has been often re-parameterized [15, 16, 75, 76] to fit different requirements, particularly in molecular computations. The atomic correlation energies obtained from HF functions compared with experimental data, or using Wigner type corrections, or the Coulomb hole functionals, were once more reconsidered by Clementi and Corongiu in 1997 with a new functional [96] aimed at an estimate of correlated non relativistic energy for the atoms and ions, ground and excited states from $Z = 2$ to $Z = 54$ (He–Xe). The progress of computational techniques and the electronic computer development (since Clementi's early 1960 HF computations) allowed eventually for systematic ab initio computations of relativistic and non-relativistic atomic energies to ground state atoms and ions from $Z = 2$ to $Z = 18$ [97].

In the early 1960s, to extend the Coulomb hole concept from atomic to molecular systems it was first of all necessary to have HF functions, thus the need to write a general HF molecular computer code [98, 99], subsequently, several times improved and re-adapted to follow the computer hardware evolution.

These post HF approximations, from Wigner, to Slater, to Clementi, denoted the DFA, should not be confused with the Density Functional Theory (DFT) approximations (see below). Unfortunately, the notation "Wigner-type density functional", used by Clementi in the last 40 years has contributed to the incorrect assumption that DFT is the only proposal in quantum chemistry using density functionals.

We recall that the Thomas-Fermi [64, 65] approximation for atomic systems, was based on the Poisson equation, and therefore relates energy and density via a simple functional; the atomic total energy is given by the simple relation $E = kZ^{3/7}$ with k a numeric constant. Despite its appealing simplicity this approximation was disregarded in the early development of quantum chemistry, due to the opinion that a classically derived relation could not lead to any molecular binding. In the late 1950s there was a renewed interest [100] and today we know that about 50% of the molecular binding can be obtained with classical considerations without inclusion of the exchange term [101].

In the mid-1960s, Hohenberg and Kohn published a theorem [102] proposing the existence of a unique relation between exact electronic density and exact wave functions for non degenerate states (thus a theorem limited to semi-classical systems), without, however, providing any explicit algorithm linking density and electronic energy. The Thomas-Fermi model was resumed as starting point in the proposal by Kohn and Sham [102], and two avenues were presented. The first one is a typical DFA approach, which re-proposes concepts published in the Coulomb hole work and "xα" approximations [92–95]; the resulting orbitals are standard AO or MO orbitals, now called Kohn–Sham orbitals. This approximation was later applied to semi-empirical molecular computations, the so called Kohn–Sham DFT approximation, popularized for example by Parr and Yang volume [54] but mostly by the availability of easy to use computer codes [104, 105]. We are of the opinion that "Kohn–Sham DFA" rather than "Kohn–Sham DFT" is most likely the correct label for the approach. The second DFT avenue [102] proposes the Hohenberg and Kohn theorem as the base for a new way to obtain exact energies, from exact densities, constrained, however, by the availability of an exact exchange expression; till today there is no such exact exchange. Rather critical for the DFT proposals are the computations of excited states, since these require vector coupling coefficients, which, however, are obtained assuming HF wave function. Today there is a wide acceptance of algorithms brutally mixing fractions of HF and DFT energies, neglecting the logical contradiction implicit in mixing energies based on wave function formalism with those based on Kohn–Sham density formalism.

Parallel to these development based on the variational method, the introduction of perturbation methods in 1934 by Møller and Plesset [46] opened new avenues, leading eventually to the Coupled Cluster methods [47, 48] complementing the variational approaches; more recently we have witnessed a merging of these approaches, for example the perturbation theory has been utilized in CASSCF computations yielding the CASPT2 method [36].

However, none of the above methods is adequate to provide an ab initio computationally efficient solution of the Schrödinger equation from short internuclear distances to dissociation. Indeed, it does not surprise that in the meantime semi-empirical models, "magic formulae" to use Mulliken expression [106], are very popular among pragmatic chemists, a consequence of the realization that quantum chemical computations should provide predictions and explanations in many facets of chemistry not only for small molecules (2–100 atoms, the classical ab initio chemistry area) but also for larger molecular systems with thousands of atoms.

4 HF and HL computations for diatomic molecules

In this section, we report computational results on diatomic molecules obtained from the HF and the HL methods. We start by recalling the definitions of Ψ_{HF} and Ψ_{HL} wave functions using the obvious notation:

$$\Psi_{\mathrm{HF}} = \det(\Phi_1, \ldots, \Phi_i, \ldots, \Phi_n) \tag{8}$$

$$\Psi_{\mathrm{HL}} = \mathrm{AN}\left[\varphi'_1(1)\ldots\varphi'_n(\mathrm{n})\Theta^{\mathrm{SM}}(1,2,\ldots,n)\right] \tag{9a}$$

$$= \Sigma_k \det(\varphi_{1k}, \ldots, \varphi_{\mathrm{i}k}, \ldots, \varphi_{mk}) \tag{9b}$$

Above, ϕ_i refers to ith HF molecular spin-orbital, φ'_i to the ith atomic orbital and and ϕ_{ik} to the ith atomic spin–orbital for the kth determinant in the HL function. AN denotes the anti-symmetry spin operator and the normalization constant, Θ^{SM} refer to the spin eigen-functions; note that the HL functions discussed in our work are constructed to satisfy the correct spin coupling constrains [107] to ensure correct dissociation states. We shall use in general the notation of Eq. 9b.

Diatomic molecules provide the simplest examples of chemical bond, in addition there is a large body of experimental data on the ground and excited state energies, and therefore are an optimal testing ground for analyzing the merits of theoretical and computational proposals to predict the molecular electronic structure. In this work, we compare HF and HL computations for the homopolar and the hydrides molecules of the first and second rows of the periodic table.

In our computations, we have used basis set of gaussian type, sufficiently large and flexible to ensure the HF and the HL limit of accuracy and to yield CI energies approaching exact non relativistic energies. We use the following basis sets: for the H atom [10,5,4/6,5,4] in the hydrides and [4, 5, 10] in the H_2 and HeH molecules; for the He atom [2, 5, 8, 9, 14]; for the Li atom [15,10,6,1/10,8,6,1]; for the Be atom [17,8,6,3/11,8,6,3]; for the B atom [15,11,7,5/9,8,6,4]; for the C atom [17,13,6,5/11,8,5,4]; for the N and O atoms [17,13,5,4/9,7,5,4], and for the F atom [18,13,5,4/12,6,5,4]. These basis sets yield the Hartree–Fock atomic ground state energies given in last column of Table 1.

In Table 1, we report molecular data for the homopolar molecules of the first and second periods: the laboratory binding energy (kcal/mol), E_{b}, the laboratory equilibrium

Table 1 Molecular and atomic data for homopolar molecules: laboratory binding energy (kcal/mol), *Eb* equilibrium distance (bohr), *Re* equilibrium total non-relativistic energy (hartree) $E_T(Re)$; same at dissociation, $E_T(R_\infty)$. Atomic ground states: Hartree–Fock atomic energy at the Hartree–Fock limit, E_{HF} (limit) and computed with the basis sets of this work, E_{HF} (this work)

Molecule	E_b[a]	Re[a]	$-E_T[Re]$	$-E_T[R_\infty]$[b]	$-E_{HF}$ (limit)	$-E_{HF}$ (this work)
$H_2\ [^1\Sigma_g^+]$	109.48[c]	1.40	1.1744757	1.000000	H $[^2S]$ 0.500000	0.499999
$He_2[^1\Sigma_g^+]$	0.02[d]	5.62	5.807483	5.807448	He $[^1S]$ 2.861680	2.861679
$Li_2[^1\Sigma_g^+]$	24.67	5.0510	14.99543	14.95612	Li $[^2S]$ 7.432727	7.432721
$Be_2[^1\Sigma_g^+]$	2.40[e]	4.63	29.33860	29.33477	Be $[^1S]$ 14.573023	14.573016
$B_2[^3\Sigma_g^-]$	68.49[f]	3.0047	49.41695	49.30780	B $[^2P]$ 24.529061	24.529036
$C_2[^1\Sigma_g^+]$	147.85[g]	2.3480	75.9256	75.6900	C $[^3P]$ 37.688619	37.688616
$N_2[^1\Sigma_g^+]$	228.4	2.0743	109.5426	109.1786	N $[^4S]$ 54.400934	54.400924
$O_2[^3\Sigma_g^-]$	120.6	2.2819	150.3270	150.1348	O $[^3P]$ 74.809398	74.809384
$F_2[^1\Sigma_g^+]$	39.0	2.6682	199.5305	199.4683	F$[^2P]$ 99.409349	99.409343
$Ne_2[^1\Sigma_g^+]$	0.08[h]	5.84	257.87673	−257.8766	Ne $[^1S]$ 128.547098	128.547052

[a] Ref. [108], [b] Ref. [97], [c] Ref. [109], [d] Ref. [110], [e] Ref. [111], [f] Ref. [112], [g] Ref. [113], [h] Ref. [114]

Table 2 Homopolar molecules. Laboratory binding energy (kcal/mol), E_b, and computed HF and HL binding energy E_b(HF) and E_b(HL), total HF and HL energies (hartree) at equilibrium E_T(HF) and E_T(HL), HF and HL correlation energies (hartree), E_C(HF) and E_c(HL)

Molecule	E_b[a]	E_b (HF)	E_b (HL)	$-E_T$ (HF)	$-E_T$ (HL)	E_c (HF)	E_c (HL)
$H_2\ [^1\Sigma_g^+]$	109.48[b]	83.83	94.28	1.133596	1.150247	0.04087	0.02422
$He_2\ [^1\Sigma_g^+]$	0.02[c]	–	–	5.723331	5.723329	0.08415	0.08415
$Li_2\ [^1\Sigma_g^+]$	24.67	3.83	8.68	14.871512	14.879239	0.12389	0.11616
$Be_2\ [^1\Sigma_g^+]$	2.40[d]	–7.54	−19.23	29.133633	29.114666	0.20458	0.12101
$B_2\ [^3\Sigma_g^-]$	68.49[e]	20.53	−15.59	49.090796	49.033188	0.32615	0.20569
$C_2\ [^1\Sigma_g^+]$	147.85[f]	18.27	−0.92	75.406347	75.375767	0.51925	0.31120
$N_2\ [^1\Sigma_g^+]$	228.4	120.15	121.96	108.993325	108.996199	0.54927	0.54640
$O_2\ [^3\Sigma_g^-]$	120.6	30.18	1.51	149.666862	149.621643	0.66014	0.70536
$F_2\ [^1\Sigma_g^+]$	39.0	−29.24	−17.59	198.770522	198.792681	0.75841	0.73942
$Ne_2\ [^1\Sigma_g^+]$	0.08[g]	–	–	257.094010	257.094008	0.78272	0.78272

[a] Ref. [108], [b] Ref. [109], [c] Ref. [110], [d] Ref. [111], [e] Ref. [112], [f] Ref. [113], [g] Ref. [114]

distance (bohr), *Re*, the total molecular non-relativistic energy (hartree) at equilibrium, $ET(Re)$, and at dissociation, $E_T(R_\infty)$. In the two last columns of the table we report atomic data: the ground state Hartree–Fock energy limit, E_{HF}(limit) and the HF atomic energy (hartree) we have computed with the above basis set, E_{HF} (this work). The molecular non-relativistic energies $E_T(R_\infty)$ are the carefully estimated atomic energies by Chakravorty et al. [97], and the total non relativistic energies $E_T(Re)$ at equilibrium are obtained by adding E_b to $E_T(R_\infty)$. In this notation, E_b includes the zero point energy.

Table 2 complements the data of Table 1 reporting the binding energy (kcal/mol) obtained from the HF and HL computations, E_b(HF) and E_b(HL), respectively and the corresponding total energies (hartree) E_T(HF) and E_T(HL) and the correlation energy E_c(HF) and E_c(HL). The different values for E_c(HF) and E_c(HL) clearly show that the correlation energy is model dependent.

For the hydrides of the first and second period, Table 3 reports: laboratory binding energies (kcal/mol), E_b, internuclear equilibrium distances (bohr), *Re*, exact non relativistic energies (hartree) at equilibrium, $E_T(Re)$ and at

Table 3 Diatomic hydrides: laboratory binding energies (kcal/mol), E_b, equilibrium internuclear separation Re (bohr), total non-relativistic energies (hartree) at equilibrium $E_T(Re)$ and $E_T(R_\infty)$ at dissociation $E_T(R_\infty)$, computed binding energies (kcal/mol), E_b(HF) and E_b(HL), from HF and HL, and corresponding correlation energy for HF and HL methods

	E_b[a]	Re[a]	$-E_T\ (Re)$	$-E_T\ (R_\infty)$	E_b (HF)	E_b (HL)	E_c (HF)	E_c (HL)
$H_2\ [^1\Sigma_g^+]$	109.48[b]	1.4[b]	1.1744757	1.000000	83.84	94.28	0.040872	0.024221
HeH $[^2\Sigma^+]$	0.01[c]	7.00	3.4037459	3.4037243	−0.0	−0.0	0.042090	0.042090
LiH $[^1\Sigma^+]$	58.00	3.0150	8.070491	−7.978062	34.27	43.11	0.083153	0.069076
BeH $[^2\Sigma^+]$	49.83[d]	2.5371	15.246772	15.167363	40.2*	−29.25	0.093607	0.220307
BH $[^1\Sigma^+]$	84.1[e]	2.3289	25.28795	25.15393	63.35	72.18	0.156363	0.143840
CH $[^2\Pi]$	83.9	2.1163	38.47869	38.34499	57.14	65.82	0.199026	0.185177
NH $[^3\Sigma^-]$	80.5[f]	1.9582	55.21754	55.08925	48.59	57.30	0.239185	0.225298
OH $[^2\Pi]$	106.6	1.8324	75.73708	75.5672	70.16	72.26	0.315893	o.311645
FH $[^1\Sigma^+]$	141.5[g]	1.7325	100.4592	100.2337	101.23	92.17	0.388535	0.400952

[a] Ref. [108], [b] Ref. [109], [c] Ref. [115, 116], [d] Ref. [117], [e] Ref. [118], [f] Ref. [119], [g] Ref. [120]

* 50.29 kcal/mol, without correction for state crossing (see Ref. [40])

dissociation $E_{T(\infty)}$; binding energies (kcal/mol) from HF and HL, E_b(HF), E_b(HL), and correlation energies (hartree), E_c(HF) and E_c(HL).

These tables exemplify the variable reliability of the HF and HL methods: qualitative agreement for most cases but also occasional inability to show any binding. The computed binding energies for the diatomic hydrides vary in accuracy from 60% for the HL model to 70% for the HF, respectively (the BeH interaction is repulsive by 29 kcal/mol in HL and it contributes to the percent with a negative value). For the homopolar diatomic molecules the HF and HL computations yield 48 and 32% of the experimental binding, respectively (F_2 is repulsive in the HF model and the same holds for B_2 and F_2 in the HL model).

Therefore, in a few situations the two classical quantum chemical models, HF and HL, fail to provide a theory capable of predicting (even qualitatively) the forces responsible for holding together atoms in a molecule. It follows that neither one of the two models can be chosen as a general zero-order approximation for quantum chemistry, namely a "reference function" which qualitatively approximates laboratory data consistently and with comparable accuracy at any internuclear separation.

Relativistic corrections are neglected for the molecules we consider in this work, since sufficiently small for the present binding energy target accuracy. The Born–Oppenheimer approximation is accepted as a reasonable approximation.

5 Decomposition of correlation effects

In previous publications [41, 43] we have analyzed in detail several decompositions of the correlation energy. The standard Löwdin definition on the correlation energy [121, 122] relates specifically to the HF method, but, since we are considering not only the HF model but also the HL and the HF–HL, we need a more general definition and an appropriate notation.

In general, the correlation energy, $E_{c,M}$, is defined relatively to a model M, yielding a total energy E_M; $E_{c,M}$ is defined as the difference between the exact non-relativistic energy E_{nr} and E_M, namely $E_{c,M} = E_{nr} - E_M$.

In a more general way, the correlation energy for a system of n electrons can be defined with reference to an exact expansion into exact one-, two-,…,n-electron energies, E_1, E_2,…,E_n. The approximated solution E_M from the model M (like E_{HF}, or E_{HL} or $E_{HF\text{-}HL}$) compared to E_1 brings about an energy difference ($E_1\ - E_M$) called "non-dynamical" correlation, $E_{c,nd,M}$; by construction $E_{c,M} = \Sigma_i E_i$ is the "total" correlation energy of the model M. The difference between $E_{c,M}$ and $E_{c,nd,M}$ is, by definition, the "dynamical" correlation energy, $E_{c,d,M}$. In conclusion, we partition $E_{c,M}$:

$$E_{c,M} = E_{c,nd,M} + E_{c,d,M} \tag{10}$$

In the following, we drop the subscript M, unless needed.

Physically, as below explained in more detail, the non-dynamical correlation can be seen as the result in the model M of "obvious errors" mainly in writing the electronic configuration, like for example the incorrect use of only one specific electronic configuration (if there are several competing near degenerate configurations) or when the model constrains two distinct electrons to have the same space–orbital leading to grossly incorrect dissociation, or when the wave function neglects to be at a crossing of two electronic state. It follows that the dynamical correlation can be considered as the true correlation correction, resulting mainly from the Coulomb hole effects.

A second partitioning is used in the HF–HL strategy. Considering the HL approach, we stress the notion that molecules are composed of atoms, and in this case the correlation energy can be broken down into two main components: one, $\Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a}}$, is the sum of the correlation corrections, ε_{a}, of each individual atom at dissociation and the second, $\eta_{\mathrm{M}} = (E_{\mathrm{c,M}} - \Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a}})$, is the “molecular extra-correlation energy”, namely the variation in the correlation due to different electronic coupling of electrons at dissociation and in the molecule. Actually, this definition was introduced in the early 1960s considering the HF molecule [123]. This viewpoint (complementary to the one in the previous paragraph) leads to:

$$E_{\mathrm{c,M}} = \Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a}} + \eta_{\mathrm{M}} \tag{11}$$

The non-dynamical correlation errors in the HF model are due to (1) neglect of near-degeneracy, (2) the constraint of doubly orbital occupancy for molecular systems approaching dissociation, (3) neglect of avoided curve crossing.

Let us consider near-degeneracy and $E_{\mathrm{c,nd,M}}$ in more detail. The non-dynamical correlation has been accounted in atoms by Hartree et al. [29] with a two term MC expansion for the near-degenerate configurations $1s^22s^22p^n$ and $1s^22s^02p^{n+2}$. Later, a different approach not limited to near-degeneracy and based on perturbation methods, was proposed by Sinanoglu [124, 125] leading essentially to the same numerical result obtained by Hartree [29], thus Hartree near-degeneracy becomes Sinanoglu non-dynamical correlation. Shortly after, following Hartree et al. [29] Veillard and Clementi [30, 31] computed with Slater-type functions $E_{\mathrm{c,nd}}$ for the second-row atoms and ions using a MC expansion of two configurations, the ground state configuration $1s^22s^22p^n$ and its near-degenerate $1s^22s^02p^{n+2}$.

Note that above we have considered configurations differing in the quantum number l but with the same quantum number n; we, therefore, talk of $nl \rightarrow nl'$ near-degeneracy. In this work, we extend the near-degeneracy concept from $nl \rightarrow nl'$ to $nl \rightarrow n'l'$ near energy excitations, generally with the constraint $n' = n + 1$ (or an integer near to n). Examples are $1s^1 \rightarrow 2s^1$ or $1s^1 \rightarrow 2p^1$ for molecules with an H atom, or equivalent excitation of valence electrons, like $2p \rightarrow 3s$ for the neon atom, as first demonstrated by Bagus et al. [126]. In the same spirit we can include molecular excitations $\sigma \rightarrow \pi$, $n\sigma_{\mathrm{g}} \rightarrow n\sigma_{\mathrm{u}}$ and $n\pi_{\mathrm{u}} \rightarrow n\pi_{\mathrm{g}}$ as “nearly degenerate” configurations.

Concerning the constraint of doubly orbital occupancy, we recall that the HF model approaching dissociation leads to grossly incorrect energies. The use of the unrestricted HF algorithm avoids this catastrophic behavior, but the resulting wave function is incorrect. An alternative, proposed by Lie et al. [15, 16] is to determine a short MC function, ensuring correct dissociation, thus gaining most of the non dynamical correlation energy. This approach marks the first computation in quantum chemistry using density functionals—in the DFA spirit—to correct MC rather than HF functions.

A third source of non-dynamical correlation is related to the degeneracy at the crossing of states with the same symmetry—a situation very common in excited states, but also frequently present in ground states [9]. Note that since at the crossing of two or more interacting states there is exact degeneracy, curve crossing can be considered as a special type of near-degeneracy.

In the HL approximation, the non-dynamical correlation error is due (1) to the neglect of near-degeneracy, (2) to the constrained selection of the lowest atomic states at dissociation, and (3) to the neglect of avoided state crossing.

We now summarize the model dependent partitioning of the correlation energy. We have partitioned the total molecular correlation energy E_{C} into the sum of $\Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a}}$ and η_{M}; further recalling the partitioning into dynamical and non-dynamical component we write:

$$E_{\mathrm{c,M}} = \Sigma_{\mathrm{a}}\left[\varepsilon_{\mathrm{a,M,d}} + \varepsilon_{\mathrm{a,M,nd}}\right] + \eta_{\mathrm{M,d}} + \eta_{\mathrm{M,nd}} \tag{12}$$

Since the correlation errors are model dependent, we distinguish the correlation correction in the HF, HL and HF–HL models and we write:

$$E_{\mathrm{c.HF}} = \Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a,HF,nd}} + \Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a,HF,d}} + \eta_{\mathrm{HF,nd}} + \eta_{\mathrm{HF,d}} \tag{13a}$$

$$E_{\mathrm{c,HL}} = \Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a,HL,nd}} + \Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a,HL,d}} + \eta_{\mathrm{HL,nd}} + \eta_{\mathrm{HL,d}} \tag{13b}$$

$$E_{\mathrm{c,HF-HL}} = \Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a,HF-HL,d}} + \eta_{\mathrm{M,HF-HL,d}} \tag{13c}$$

Equation 13c results from the realization (see next section) that sum $\Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a,nd}} + \eta_{\mathrm{M,nd}}$ is accounted by construction in the HF–HL method. Equation 13c is the basic equation in the HF–HL model: $\eta_{\mathrm{M,HF\text{-}HL,d}}$ is computed ab initio with a relatively few term expansion, and $\Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a,d}}$ is closely approximated with a simplified form of the Coulomb hole functional (mainly a scaling of the molecular energy to ensure correct non relativistic atomic energies).

We add a short comment on notation. Above we have introduced definitions and a specific notation for the HF–HL method. We indicate as $\mathrm{MC_{HF}}$ and $\mathrm{MC_{HL}}$ multi-configuration expansions of HF and HL type functions, respectively. When needed, we use the specific notation HF(n), HL(m) and HF–HL(n, m) to designate $\mathrm{MC_{HF}}$ expansions of n configurations, $\mathrm{MC_{HL}}$ expansions of m configurations, and HF–HL functions composed with HF(n) and HL(m) configurations. The energies $\mathrm{E}_{\mathrm{HF}(n)}$, $\mathrm{E}_{\mathrm{HL}(m)}$ and $\mathrm{E}_{\mathrm{HF\text{-}HL}(n,m)}$ correspond to the wave functions $\Psi_{\mathrm{HF}(n)}$, $\Psi_{\mathrm{HL}(m)}$ and $\Psi_{\mathrm{HF\text{-}HL}(n,m)}$, respectively. Equivalent notation is used for the computed binding energies, E_{b}, and the correlation energies, $\mathrm{E_c}$.

6 The HF–HL model

The HF–HL method (1) accounts by construction for the non dynamical correlation energy resulting from the HF incorrect dissociation, thus provides the correct dissociation, (2) solves ab initio for the HF–HL molecular extra correlation energy, $\eta_{\mathrm{M,HF\text{–}HL,d}}$ of Eq 13c, (3) accounts via a density functional for the dynamical correlation of the components atoms, $\Sigma_{\mathrm{a}}\varepsilon_{\mathrm{a,\ HF\text{–}HL,d}}$ of Eq. 13c.

Formally, we start with the Ψ_{HF} and the Ψ_{HL} functions, previously given in Eq. 8 and 9. The HF–HL wave function $\Psi_{\mathrm{HF\text{–}HL}}$ is obtained by determining variationally the linear combination

$$\Psi_{\mathrm{HF-HL}} = c_1\Psi_{\mathrm{HF}} + c_2\Psi_{\mathrm{HL}} \tag{14}$$

When at dissociation the atoms in the molecule are in a state with near-degeneracy (e.g., $nl \rightarrow nl'$ and/or when there is avoided crossing, then Ψ_{HF} and Ψ_{HL} are replaced with short MC expansions, accounting for near-degeneracy and avoided crossing:

$$\Sigma_{\mathrm{t}} a_{\mathrm{t}} \Psi_{\mathrm{HF}}(t) = \Sigma_{\mathrm{t}} a_{\mathrm{t}} \left[\det(\Phi_1, \ldots, \Phi_i, \ldots, \Phi_n)_t\right] \tag{15a}$$

$$\Sigma_{\mathrm{p}} b_{\mathrm{p}} \Psi_{\mathrm{HL}}(sp) = \Sigma_{\mathrm{p}} \mathrm{b}_{\mathrm{p}} \Sigma_{\mathrm{k}} [\det(\varphi_{1\mathrm{k}}, \ldots, \varphi_{\mathrm{ik}}, \ldots, \varphi_{\mathrm{mk}})]_{\mathrm{p}} \tag{15b}$$

where the a_{t} and b_{p} are the weights of the expansions. The corresponding HF–HL wave function, $\Psi_{\mathrm{HF\text{-}HL}}$, is obtained by determining variationally the linear combination

$$\Psi_{\mathrm{HF-HL}} = \Sigma_{\mathrm{t}} a_{\mathrm{t}} \Psi_{\mathrm{HF}}(t) + \Sigma_{\mathrm{p}} b_{\mathrm{p}} \Psi_{\mathrm{HL}}(p) \tag{16}$$

In the HL component all spin couplings are considered [107] and therefore the function dissociates into atoms in the correct state.

In Eq. 16 the a_{t} and b_{p} coefficients are obtained variationally by solving the equation

$$(\mathbf{H} - \mathbf{SE})\mathbf{C} = 0 \tag{17}$$

with **H** and **S** the interaction super-matrices containing the Hamiltonian and the overlap matrix elements, respectively. The ϕ_{i} orbitals of Ψ_{HF} are linear combination of a basis set either of gaussian or Slater type functions and the same basis set is also used to expand the orbital φ_{lk} of the Ψ_{HL} component. We recall that the ϕ_{i} orbitals form an orthogonal set, whereas the φ_{lk} orbitals are generally non-orthogonal. In the latter case, following a general method proposed by Löwdin [121] and later reinterpreted by Slater [127], the interaction between two determinants, d_{a} and d_{b}, is given by:

$$\langle d_{\mathrm{a}}|H|d_{\mathrm{b}}\rangle = \sum_{ij} h_{ij} S^{(i,j)} + \sum_{i,l<k,j} \langle \mathrm{l}[\langle \mathrm{ij}|\mathrm{kl}\rangle - \langle \mathrm{il}|\mathrm{kj}\rangle] S^{(i,k,j,l)} \tag{18}$$

where the indices i and k refer to the occupied orbitals of d_{a} and j and l to those of d_{b}; $S^{(i,j)}$ and $S^{(i,k,j,l)}$ are the first and second order cofactors of the overlap matrix **S**, constructed with the occupied orbitals of d_{a} and d_{b}. The bi-orthogonal transformation is an effective way to compute the cofactors [128], but matrix element evaluation is computationally demanding. Therefore, a number of simplifying techniques have been proposed [129, 130]. For example, Leasure et al. [131] combined determinant properties and the bi-orthogonal transformation to produce an efficient evaluation of all the matrix elements, thus reducing the complexity of the original Löwdin formulation.

In our approach, we first define the chosen HF configurations and HL structures expanded with a unique basis set of N basis functions. Next, we apply an integral transformation from the basis set integral list, to molecular and atomic orbitals and relative cross terms between molecular and atomic functions. With algorithms reported in VB literature [23], the matrix elements $\langle d_{\mathrm{a}}|H|d_{\mathrm{b}}\rangle$ are then computed for the interactions of HF with HF functions, of HL with HL structures, and of HF with HL structures. We then solve by diagonalization Eq. 17. To optimize the orbital expansion coefficients, we currently use a numerical algorithm based on the Newton–Raphson procedure. The present computer code is still in development [132].

In the implementation of the HF–HL method we proceed by successive steps. In the first step (referred to as "the simple HF–HL") we variationally combine standard Ψ_{HF} and Ψ_{HL} functions (see Eq. 14); the corresponding energy is $E_{\mathrm{HF\text{–}HL}}$ (1, 1). For example the binding energy of the F_2 ground state, computed in the HF and HL methods as repulsive interactions (29.24 and 17.59 kcal/mol, respectively) becomes attractive using Eq. 14 with a computed binding of 11.46 kcal/mol.

When there is near degeneracy and/or state crossing, then we add the corresponding degenerate and /or crossing configurations, yielding Eq. 16.

Since neglect of degeneracy and state crossing are "obvious errors", Eqs. 19 and 20 constitute the "simple HF–HL" model.

For example, let us consider the ground state $^1\Sigma_{\mathrm{g}}^+$ of C_2; recalling that a $C[^3\mathrm{P}]$ corresponds to a manifold of near-degenerate atomic configurations (specifically, $1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^2$, $1\mathrm{s}^2 2\mathrm{s}^1 2\mathrm{p}^3$, and $1\mathrm{s}^2 2\mathrm{s}^0 2\mathrm{p}^4$) and recalling also the Wigner–Witmer rules [74] (to obtain a $^1\Sigma_{\mathrm{g}}^+$, we can combine the $^3\mathrm{P}$, $^1\mathrm{D}$ and $^1\mathrm{S}$ states of the two carbon atoms) we realize that there are many near degenerate configurations representing C_2 $[^1\Sigma_{\mathrm{g}}^+]$. The computed binding energies from the HF, HL models and from HF–HL with Eq. 14 are 18.27, –0.92, and 41.90 kcal/mol respectively; computation from HF–HL with Eq. 16 brings the binding to 127.10 kcal/mol, not far from the experimental value of 147.85 kcal/mole. We stress that for carbon chemistry the near degeneracy is a factor of paramount importance in determining stability; in Sect. 9 we shall see in addition that the near-degeneracy is very important also for the correct determination of excited state energies.

In a following step, we add to $\Sigma_p b_p \Psi_{HL}(p)$ of Eq. 16 a number of ionic structures designated $\Sigma_i b_i \Psi_{HL}$ (1): this yields the "HF–HL ionic mode" designated "HF–HL–i":

$$\Psi_{HF-HL-i} = \Sigma_t a_t \Psi_{HF}(t) + \Sigma_p b_p \Psi_{HL}(p) + \Sigma_i b_i \Psi_{HL}(i) \quad (19)$$

where the coefficients a_t, b_p and b_i are obtained as above explained; the corresponding energy is $E_{HF-HL-i}$. Note that generally we use few $\Psi_{HF}(t)$ terms (often only one), since more and more redundant by the presence of the $\Psi_{HL}(p)$ and $\Psi_{HL}(i)$ expansions. To illustrate Eq. 19 we consider as examples the binding energies in F_2 and C_2: the computed HF–HL–i binding energies are 37.43, and 147.35 kcal/mol, respectively, an indication that consideration of ionic structures is essential to obtain realistic binding energies.

In general, we include the $nl \rightarrow nl'$ near degenerate configurations (structures) at the early stage of the computation, and $nl \rightarrow n'l'$ near excitations at the end of the computation, after solving for Eq. 19; further we can re-optimize Ψ_{HF} in Eq. 19 in the field of other components of $\Psi_{HF-HL-i}$. In this paper, we indicate the inclusion of $nl \rightarrow n'l'$ near energy excitations and, eventually, the re-optimization of Ψ_{HF} with the notation $\Psi^*_{HF-HL-i}$. This extension allows inclusion of promotions to orbitals with different symmetry, an essential step to obtain accurate binding energies. The Eq. 20, namely inclusion of selected excited MC–HF (designated Ψ^*_{HF}) and MC-HL (designated Ψ^*_{HL}) non orthogonal configurations, represents a final refinement in the computation of the binding energy:

$$\Psi^*_{HF-HL-i} = \Sigma_r a_r \Psi^*_{HF}(r) + \Sigma_s b_s \Psi^*_{HL}(s) + \Sigma_i b_i \Psi_{HL}(i) \quad (20)$$

To illustrate Eq. 20 we consider the water molecule; the computed HF, HL, HF–HL–i binding energies are 161.84, 166.04, and 208.43 kcal/mol, respectively; after inclusion of three additional configurations of $nl \rightarrow n'l'$ type on the hydrogen atom (leading to a total of 1,522 determinants for the $\Psi^*_{HF-HL-i}$ function) the binding energy increases to 227.69 kcal/mol, to be compared to the experimental atomization energy [133] of 232.77 ± 0.24. We are now in the process of adding $nl \rightarrow n'l'$ type configurations to the oxygen atom. (Note that Ref. [133] reports a Full CI/cc-pVTZ basis set computation requiring 1.7 x 10^9 determinants and yielding a binding energy of 216.29 kcal/mol.) As a second example we consider the hydride OH; addition of H atomic configurations with a 2 s orbital brings about a binding energy increase from 98.11 kcal/mol—the HF–HL–i result—to 106.9 kcal/mol, the latter to be compared with a recommended experimental value [133] of 107.1 kcal/mol. As third example, we consider a computation on F_2 with an HF–HL–i binding of 36.12 kcal/mol increases to 38.71 kcal/mol with the addition of one $nl \rightarrow n'l'$ configuration, not far from the experimental value [108] of 39.0 kcal/mol.

At this stage the binding energy is accounted for and to obtain the total correlation correction we must account only for the dynamical correlation of the atomic components, $\Sigma_a \varepsilon_{a,HF-HL,d}$. This is accomplished for example by the use of the Coulomb hole DFA, described in Sect. 3, which simply corresponds to a total energy shift (scaling); computational results are given in the following section.

In Table 4 we list the number of determinants used in Eqs. 14, 16 and 19 for the homopolar and hydride diatomic molecules we have considered in this work. The reported expansion length is notably shorter than that needed in CI or CASSCF wave function computations, with the same basis set and equivalent active space. We have not determined a general scaling rule on the number of determinants for a given number of active electrons, due to the complication generated by the inclusion of near-degeneracy. However it is clear that the scaling increases rapidly with the number of binding electrons, unless the spin functions

Table 4 Number of determinants in simple HF–HL computations using Eq. 14 (without near-degeneracy), or from Eq. 16 (with near-degeneracy), or from Eq. 19 (HF–HL–i model)

Molecule	Equation 14	Equation 16	Equation 19	Molecule	Equation 14	Equation 16	Equation 19
H_2 $[^1\Sigma_g^+]$	3	–	5	LiH $[^1\Sigma^+]$	3	–	5
Li_2 $[^1\Sigma_g^+]$	3	–	5	BeH $[^2\Sigma^+]$	2	8	10
$Be_2[^1\Sigma_g^+]$	3	133	436	BH $[^1\Sigma^+]$	3	13	15
B_2 $[^3\Sigma_g^-]$	3	511	527	CH $[^2\Pi]$	6	21	31
C_2 $[^1\Sigma_g^+]$	13	535	781	NH $[^3\Sigma^-]$	10	–	39
C_2 $[^3\Pi_u]$	18	565	–	OH $[^2\Pi]$	6	–	8
C_2 $[^3\Sigma_g^-]$	18	565	–	HF $[^1\Sigma^+]$	3	–	8
N_2 $[^1\Sigma_g^+]$	91	–	183	CO $[^1\Sigma^+]$	30	302	758
O_2 $[^3\Sigma_g^-]$	25	–	39	H_2O* $[^1A]$	39	–	104
F_2 $[^1\Sigma_g^+]$	3	–	9	BF $[^1\Sigma^+]$	3	12	46

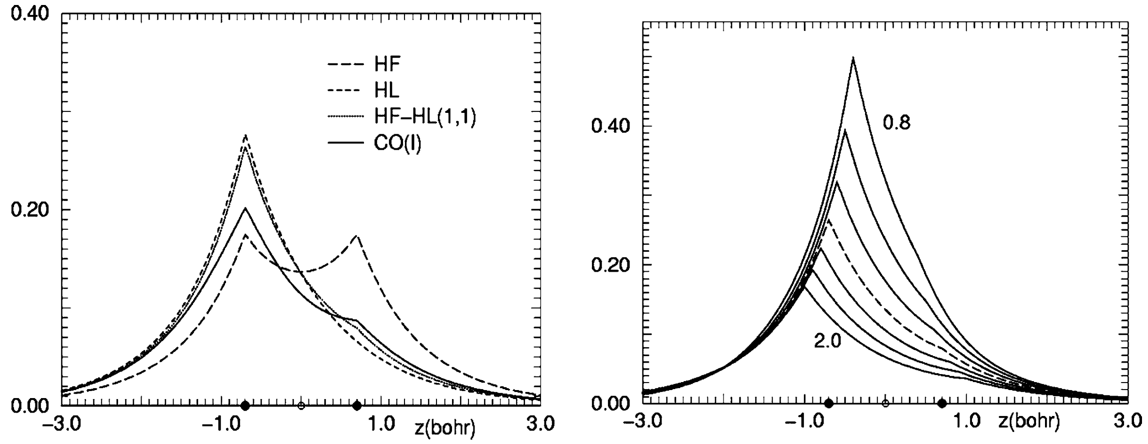

Fig. 1 Wave function for the H_2 molecule *Left* from Ψ_{HF}, Ψ_{HL}, $\Psi_{HF\text{–}HL}$ and Ψ_{CO} models at equilibrium separation (see text). *Right* $\Psi_{HF\text{–}HL}$ function for different internuclear separations, starting at $R = 2.0$ bohr and decreased by 0.2 to the value $R = 0.8$ bohr

are limited to specific bonds. Algorithms based on dissociation into groups of atoms (fragments) rather than into the component atoms might offer a solution.

In Fig. 1 we plot the electronic functions, $\Psi(0., 0., z_1; 0., 0., z_2)$, for H_2 computed at the internuclear separation of 1.4 bohr, obtained from the HF, HL and HF–HL models (left inset) and for the HF–HL model at seven different internuclear separations, from 2.0 to 0.8 bohr (right inset). Note that we include in the figure also the representation from a new wave function, designated Ψ_{CO}, described in Sects. 10–12.

In the insets we indicate with an empty dot the internuclear midpoint separation, with full dots the nuclear positions for nucleus A at $z = -0.70$ and nucleus B at $z = 0.7$. Electron 1 is fixed at the midpoint on the internuclear axis of the molecule, $z_1 = 0.0$. The function for electron 2 is plotted from $z_2 = -3.0$ to $z_2 = 3.0$ bohr. The left inset shows that the electronic function is symmetrical for the familiar HF function, with the two maxima in correspondence of the nuclei A and B. For the HL function the plot shows the familiar maximum in correspondence of one of the nuclei, A. For the HF–HL function the plot is similar to that of the HL function from large (negative) distances to the nuclear position A, but it has a secondary maximum in correspondence of the nucleus B, due to the HF component in the HF–HL function (recall that for H_2 at the equilibrium position, the HL function is more important than the HF function). As we shall discuss later in Sect. 10, where we outline the Ψ_{CO} method, the secondary maximum is more developed in Ψ_{CO} relative to $\Psi_{HF\text{–}HL}$, and it increases by reducing the internuclear separation from 2.0 to 0.8 bohr with a progressive shift toward the midpoint of the bond reaching a maximum at the united atom.

In conclusion, in this section we have outlined a new method, the HF–HL, as an ab initio technique in molecular wave function computations: we have merged traditional LCAO–MO (in the HF form) and AO–VB (in the HL form) and accounted for the molecular extra correlation correction (to obtain correct binding energies) with relatively short expansions based on physical concepts (degeneracy and ionic structures). Alternatively stated, our approach represents a conclusion of an historical path initiated in the 1930. Below, we shall test the new method by systematically computing the potential energy of first and second period diatomic hydrides and homopolar molecules (ground state and a few excited states).

Note that most of the computational techniques today available stress the "user friendliness" and the computational speed; in our method we have attempted to focus on physical effects and criteria for building the wave function.

7 HF–HL computations for homopolar and hydride diatomic molecules

The diatomic molecules previously considered with the HF and HL approximation (see Sect. 4; Tables 1, 2, 3) have been computed once more with the HF–HL method [39–43] yielding the data reported in the Tables 5, 6, 7 and 8. The corresponding potential energy curves are reported in detail in Refs [42] and [43]; note that the computed binding energy is obtained comparing the energy at equilibrium with the energy computed at very large internuclear separations (30–40 bohr), and not by summing total atomic energies obtained from different models, as it is customary in most computational chemistry papers.

For the hydride molecules we report in Table 5 the binding energy computed with the HF–HL model of Eqs. 14 and/or 16 indicated as the Eb(HF–HL) and the Eb(HF–HL–i) energies from Eq. 19, respectively, namely without and with addition of ionic structures. For Eb(HF–HL–i) we report also the total energies at equilibrium and at dissociation, $E(\text{HF–HL–i})_{Re}$ and $E(\text{HF–HL-i})\infty$, respectively.

Table 5 Diatomic hydrides: computed binding energies (kcal/mol), E_b(HF–HL), E_b(HF–HL–i), and total energies (hartree) at equilibrium, E(HF–HL–i)$_{Re}$, and at dissociation, E(HF–HL–i)R_∞

Molecule	E_b (HF–HL)	E_b (HF–HL–i)	E (HF–HL–i)$_{Re}$	E (HF–HL–i)R_∞
H_2 $[^1\Sigma_g^+]^a$	94.50	95.42^a	–1.15207	–1.00000
HeH $[^2\Sigma^+]$	–0.0	0.17	–3.37826	–3.37799
LiH $[^1\Sigma^+]$	43.66	46.59	–8.00699	–7.93274
BeH $[^2\Sigma^+]$	40.50	45.73	–15.18961	–15.11673
BH $[^1\Sigma^+]$	77.78	78.10	–25.18831	–25.06384
CH $[^2\Pi]$	70.03	78.39	–38.33102	–38.20610
NH $[^3\Sigma^-]$	60.29	71.50	–55.01548	–54.90153
OH $[^2\Pi^b]$	79.62	98.11^b	–75.46883	–75.31028
HF $[^1\Sigma^+]$	108.36	136.12	–100.12830	–99.91136

[a] H_2 the HF*–HF–HL–i yields 108.56 kcal/mol

[b] OH the HF*–HF–HL–i yields 106.9 kcal/mol

Table 6 Homopolar molecules. Binding energy (kcal/mol) from simple HF–HL without near-degeneracy, from HF–HL–i and HF*–HL–i and correlation energy (hartree) at equilibrium for HF, HL, and HF–HL–i

Molecule	E_b (HF–HL) Eq.14	E_b (HF–HL) Eq. 16	E_b (HF–HL–i) Eq. 19	E_b (HF*–HL–i) Eq. 20	E_c (HF)	E_c (HL)	E_c (HF–HL–i)
H_2 $[^1\Sigma_g^+]$	94.50	94.50	95.42	108.56	0.04067	0.02422	0.02387
Li_2 $[^1\Sigma_g^+]$	8.69	8.69	25.48	25.70	0.12389	0.11616	0.08939
Be_2 $[^1\Sigma_g^+]$	–7.53	–9.49	0.50	0.52	0.20458	0.12101	0.10433
B_2 $[^3\Sigma_g^-]$	23.05	55.01	62.95	63.77	0.32615	0.20569	0.19303
C_2 $[^1\Sigma_g^+]$	41.90	127.10	138.40	143.86	0.51925	0.31120	0.29298
N_2 $[^1\Sigma_g^+]$	159.96	175.04	213.16	220.03	0.54927	0.54640	0.40106
O_2 $[^3\Sigma_g^-]$	62.26	76.56	110.12	115.02	0.66014	0.70536	0.65350
F_2 $[^1\Sigma_g^+]$	11.46	11.46	35.70	38.71	0.75841	0.73942	0.65350

Table 7 Homopolar molecules. Computations with Coulomb hole functional: binding (kcal/mol), E_b(HF–HL)Ch, total (hartree), E_t(HF–HL)Ch–R_e, E_t(HF–HL)Ch–R_∞, errors for binding, total energy, ΔE_b (kcal/mol) and $\Delta E_{t\infty}$ (mhartree), and computed equilibrium distance (bohr), Re

Molecule	E_b(HF–HL)Ch	$-E_t$(HF–HL)Ch–R_e	$-E_t$(HF–HL)Ch–R_∞	ΔEb	$\Delta E_{t\infty}$	Re
H_2 $[^1\Sigma_g^+]$	109.48	1.17448	1.00000	0.00	0.00	1.40
He_2 $[^1\Sigma_g^+]$	0.02	5.807470	5.807436	0.00	0.00	6.25
Li_2 $[^1\Sigma_g^+]$	22.95	14.99253	14.95596	–1.74	–0.02	5.111
Be_2 $[^1\Sigma_g^+]$	2.09	29.33761	29.33427	–0.31	–0.05	4.167
B_2 $[^3\Sigma_g^-]$	66.41	49.41007	49.30423	–2.11	–3.57	3.025
C_2 $[^1\Sigma_g^+]$	147.44	75.92379	75.68883	–0.41	–1.17	2.348
N_2 $[^1\Sigma_g^+]$	227.83	109.54025	109.17717	–1.11	–1.43	2.041
O_2 $[^3\Sigma_g^-]$	116.91	150.32046	150.13415	–3.72	–0.65	2.191
F_2 $[^1\Sigma_g^+]$	39.86	199.53180	199.46827	0.86	–0.07	2.603
Ne_2 $[^1\Sigma_g^+]$	0.08	257.875856	257.875723	0.00	–0.88	6.40

Table 8 Hydride molecules. Coulomb hole computed binding energy (kcal/mol), E_b(HF–HL)–Ch, total energy (hartree) at equilibrium, E(HF–HL)–Ch(Re), and at dissociation, E(HF–HL)–Ch(R_∞), deviation, ΔE, (kcal/mol) of the latter from exact non-relativistic energies, computed equilibrium separation in bohr, Re–Ch

Molecule	E_b(HF-HL)– Ch	–E(HF–HL)–Ch(Re)	–E(HF–HL)–Ch(R_∞)	ΔE	Re–Ch
H_2 [$^1\Sigma_g^+$]	109.48	1.17447	1.00000	0.00	1.40
LiH [$^1\Sigma^+$]	59.22	8.07236	7.97798	0.05	3.01
BeH [$^2\Sigma^+$]	49.55	15.24611	15.16716	0.13	2.59
BH [$^1\Sigma^+$]	86.77	25.29208	25.15382	0.07	2.33
CH [$^2\Pi$]	82.65	38.47601	38.34429	0.44	2.11
NH [$^3\Sigma^-$]	81.57	55.21857	55.08846	0.50	1.93
OH [$^2\Pi$]	107.18	75.73765	75.56685	0.22	1.80
HF [$^1\Sigma^+$]	140.91	100.45867	100.23412	−0.26	1.68

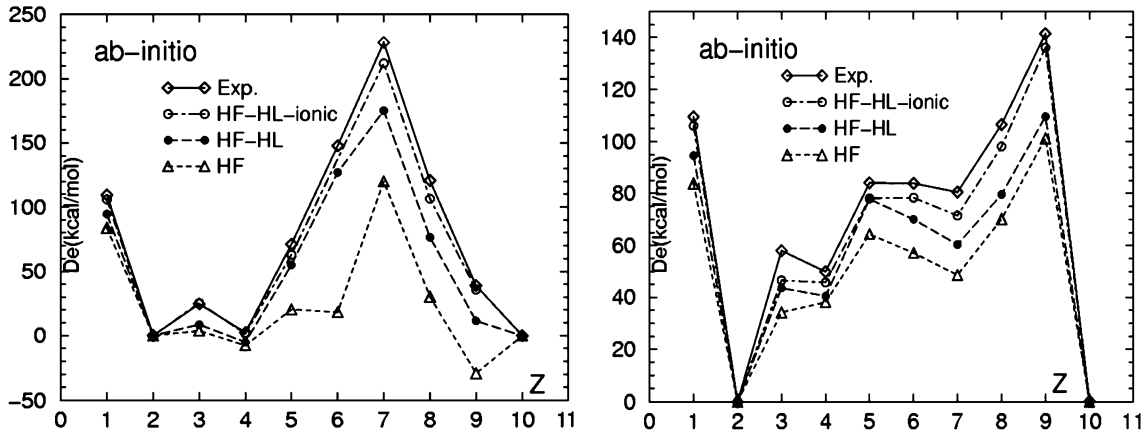

Fig. 2 Binding energy (kcal/mol): values from experiments (*Exp*) and from HF–HL–i, HF–HL, and HF computations. *Left* for homopolar molecules. *Right* for hydride molecules

In Table 6, we report for the homonuclear molecules binding energies from the HF–HL models of Eq. 14, Eb(HF–HL), Eq. 16, Eb(HF–HL), Eq. 19, Eb(HF–HL–i), and Eq. 20, Eb(HF*–HL-i). The last three columns of Table 6 report the correlation energy not accounted in the HF, HL and HF–HL–i computations.

Comparing the values of the computed binding energies obtained from the HF, HL with those from HF–HL to HF–HL–i to HF*–HL–i, the improvement is evident: this is graphically reported in Fig. 2, where the computed bindings are plotted for the homopolar molecules and for the hydrides.

The HF–HL method—in the implementation of Eq. 14 and, when applicable of Eq. 16 accounts for the non-dynamical correlation energy (near-degeneracy and explicit consideration of avoided crossing). With this simple HF–HL model without ionic structures, we have obtained in average 80% of the experimental binding energy for the hydrides, to be compared with 60 and 70% from HL and HF computations, respectively; for the homopolar diatomic molecules we obtain 66% of the experimental binding, compared to 48 and 32% from HF and HL computations.

From Tables 5 and 6 and from Fig. 2 it is evident the importance of including ionic structures in the HL component. In Refs. [42] and [43] we provide in detail the electronic configurations of the HF and HL functions needed in the HF–HL–i computations.

Note that the so called "ionic structures" raise the physical interpretation problem pointed out since the 1931 paper by Majorana [136]: charge transfer via ionic structures has no place in homopolar molecule, even if ionic structures are an efficient way to introduce "in–out" correlation. Majorana used the designation "pseudo-polar" to underline the logical difficulty; we shall continue with the use of the term "ionic structure", following the VB tradition. In Sect. 10, we shall show that ionic structures are simply the outcome of a decomposition of a new and more general wave function, Ψ_{CO}, constructed with CO.

From the HF–HL model computations on the hydrides and homopolar molecules [39–44], we have learned how to refine the computation of the binding energy, ensuring errors of less than one kcal/mol. As noted, an improvement comes about by considering not only $nl \rightarrow nl'$ *near* degeneracy, but also the $nl \rightarrow n'l'$ type excitations.

Second, there is another rather obvious potential improvement which is associated with the use of a larger number of polarization functions in the basis set. Indeed since long ago it is well known that very accurate atomic [134] and molecular [135] computations need functions of high angular momentum, not only 4f but also, 5 g, 6 h and 7i (at the cost of a non trivial increase in computer time).

8 Computation of the atomic dynamical correlation energy, $\Sigma_a\varepsilon_{a,d}$

Once the HF–HL wave-function is obtained by solving for Eqs. 16 and 19 the largest remaining correlation error is $\Sigma_a\varepsilon_{a,d}$ (see Eq. 13c). Since $\varepsilon_{a,d}$ is a simple and regular function of the atomic number *Z*, the computational task is not as complex as in DFT computations, and it can be accomplished using the Soft Coulomb hole, Ch, DFA [92, 137, 138].

The computed binding energies, using the Coulomb hole functional are displayed in Fig. 3 and collected in Tables 7 and 8. Let us consider first the homopolar molecules. Table 7 reports the computed binding energy at equilibrium, E_b(HF–HL)–Ch, the total energy at equilibrium, E_T(HF–HL)–Ch–R_e, and dissociation, ET(HF–HL)–Ch–R_∞, the error in the computed binding energy, ΔE_b, and in the total energy at dissociation, $\Delta E_{t\infty}$, relative to accurate non relativistic values (see Table 1), and the equilibrium distance, R_e. The data from the computed binding energy either from E_b(HF–HL–i) or from E_b(HF–HL)–Ch shows that the computational technique we have proposed yields reliable values. There are deviations from experiments, particularly for Be_2 and O_2, but the overall resulting trend is satisfactory.

To complete the tabulation for the homopolar molecules we add very preliminary computations for He_2 and Ne_2, the (HF–HL) (1,1) total energies (in hartree) at the experimental equilibrium separation and at dissociation are −5.723331 and −5.723359 for He_2 and −257.094010 and −257.094104 for Ne_2. The computations with HF–HL–Ch (see Table 7) show a minimum, but at larger internuclear separation then experimentally observed.

Let us now consider the hydrides. The data obtained with the DFA Coulomb hole are given in Table 8 and in Refs. [42] and [44]. In Table 8 we report the binding energy, E_b(HF–HL)–Ch, the total energy at equilibrium, *E*(HF–HL)–Ch(*Re*), and at dissociation, *E*(HF–HL)–Ch(R_∞), the deviation, $\Delta E(\infty)$, between the latter values and exact non-relativistic energies, and the computed equilibrium distance, *Re*. The deviations ΔE show that the Ch parameterization is reliable.

The data reported in the Tables allow to rationalize the variation of the binding energy molecule to molecule. Regularity in the correlation energy trends related to trends in the binding energy are discussed elsewhere [42, 44].

Presently, we are extending our work to include other diatomic molecules and also polyatomic molecules. For the molecule of water we are considering the process OH + H → H_2O, and for acetylene the process CH_2 + CH_2 → C_2H_2 (work in progress).

Concerning the computed binding energies at dissociation we recall that, due to the molecular symmetry, the 2p electrons are split into $2p_\sigma$ different from $2p_\pi$; for the

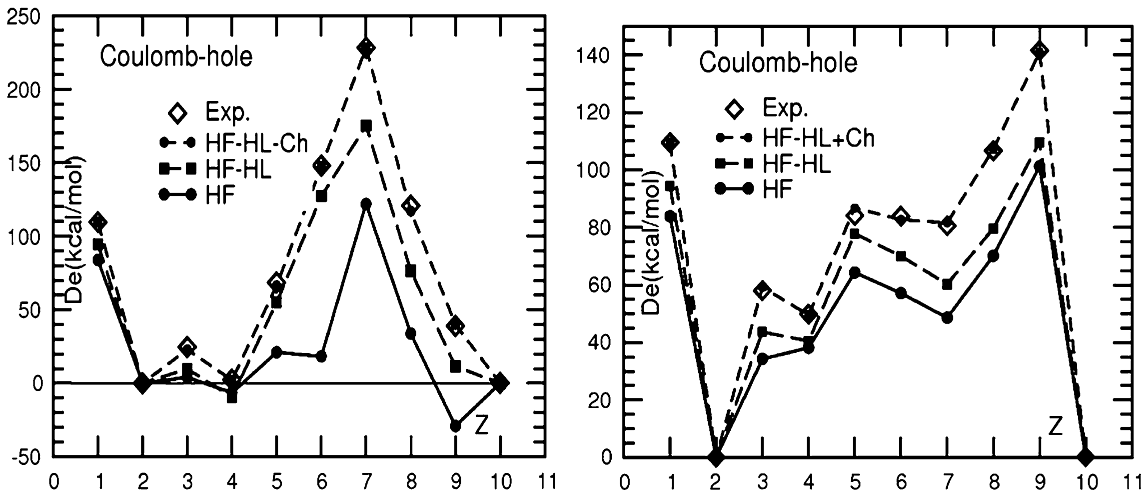

Fig. 3 Binding energy (kcal/mol): values from experiments (*Exp.*) and from HF–HL–Ch, HF–HL, and HF computations. *Left* for homopolar molecules. *Right* for hydride molecules

separated atom (in spherical symmetry) there is no such splitting. This causes some correlation energy gain (due to the use of different orbitals for different spins) in the molecule but not in the separated atoms. The energy gain is not negligible and for example amounts to ~2.5 kcal/mol in F_2. The molecular energy at a very large distance (considered "dissociation distance") matches the sum of the separated atoms by constraining the basis set coefficients of the $2p_\sigma$ orbitals to be degenerate to those of the $2p_\pi$ orbitals [43, 44] at large R values; the imposed constraint notably improves the energy matching of the linear molecular symmetry with the atomic spherical symmetry computations (compare the data at dissociation in Table 7 with the equivalent data in Table 1). The corresponding potential energy curves are given in Refs. [42] and [43].

To conclude this section, we note that the choice of the Coulomb hole algorithm is not unique and several different functionals [75] can be used. For example, we recall the extensive computations by Lie et al. for diatomic hydrides [16] and homopolar [17] molecules, where a Wigner type density functional is applied to a specific MC expansion (computed to correct the HF deficiency at dissociation), yielding reasonable binding and total energies. A study by Wang and Schwarz [139] supports these findings with formal considerations. We recall in addition that Colle and Salvetti extended the applicability of their functional [140] from HF to MC functions [141].

In Fig. 4, we report computations of the correlation correction for the HF–HL model with functionals different from the Coulomb hole functional. As examples, we compare the HF–HL computations of Eq. 14 with the Colle-Salvetti [140], CS, and the LYP [142] functionals (derived from the Colle-Salvetti) and with the very popular B3LYP [143] functional. In Fig. 4 we consider the F_2 and HF ground state molecules.

9 Excited states

Excited states are well represented by the HF–HL model, and below we provide examples for the C_2 and the LiH molecules. The computed potential energy curves are given in Figs. 5 and 6, and the data summarized in Table 9.

For C_2, we have considered the $^3\Pi_u$ and $^3\Sigma_g^-$ excited states reported in Fig. 5. Experimentally, [108, 113] the lowest state is the $^1\Sigma_g^+$, followed by the $^3\Pi_u$ with an excitation energy of 0.1 eV and then by the $^3\Sigma_g^-$ with an excitation energy of 0.96 eV . The HF–HL binding energy of the $^1\Sigma_g^+$, $^3\Pi_u$ and $^3\Sigma_g^-$ states, without inclusion of near degeneracy, is 41.90, 83.72 and 100.61 kcal/mol, respectively, to be compared to the HF values of 18.27, 72.94 and 87.34 kcal/mol and to the experimental values [108, 113] of 147.85, 143.51 and 126.91 kcal/mol. The HF–HL total energies are −75.44406, −75.51065 and −75.53767 hartree for the three states $^1\Sigma_g^+$, $^3\Pi_u$ and $^3\Sigma_g^-$, respectively.

Note the incorrect HF and HF–HL trends in the energies at these computational levels; both predict a $^3\Sigma_g^-$ ground state, followed by $^3\Pi_u$ and then by $^1\Sigma_g^+$. Inclusion of near degeneracy in the HL wave function improves the binding energies to 127.10, 124.06 and 107.30 kcal/mol with total energies of −75.61460, −75.60967 and −75.58305 hartree for the three states $^1\Sigma_g^+$, $^3\Pi_u$ and $^3\Sigma_g^-$, respectively, leading to a correct order of the excitation energies, 0.13 and 0.86 eV for the $^3\Pi_u$ and $^3\Sigma_g^-$, respectively (the 0.13 eV value improves previous MC–HF computational results discussed elsewhere [43]). The HF–HL–ch computations bring the above binding energies to 147.44, 145.29, and 127.64 kcal/mol for the three states $^1\Sigma_g^+$, $^3\Pi_u$ and $^3\Sigma_g^-$, respectively (see in Table 9 the column $E_b(C-h)$).

In Fig. 5, left inset, we display the three states without and with inclusion of near-degeneracy. Inclusion of degeneracy leads to the very reasonable result reported in Table 9; with the Coulomb hole functional correction

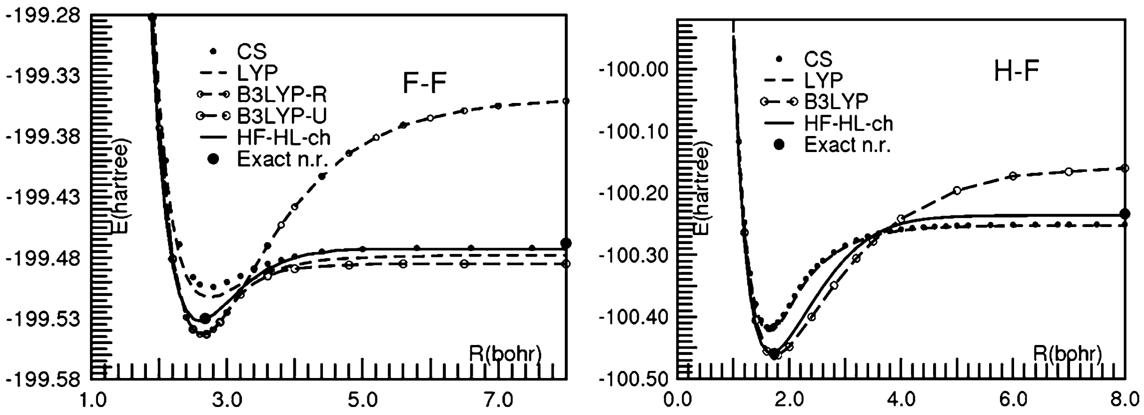

Fig. 4 F_2 and HF ground states. Coulomb Hole functional, compared to Colle–Salvetti, CS, LYP and B3LYP, restricted and unrestricted for F_2

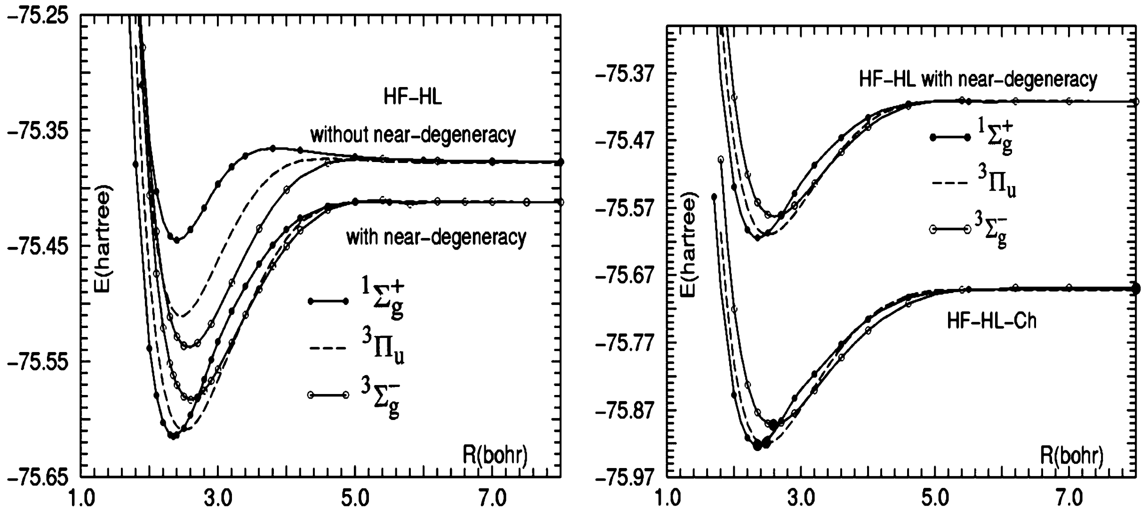

Fig. 5 Potential energy for the three lowest states of C_2. *Left* computations from HF-HL without (*top three curves*) and with near-degeneracy (*bottom three curves*). *Right* computations from HF-HL with near-degeneracy and HF–HL–Ch; bullets for the exact non-relativistic energy at equilibrium and dissociation

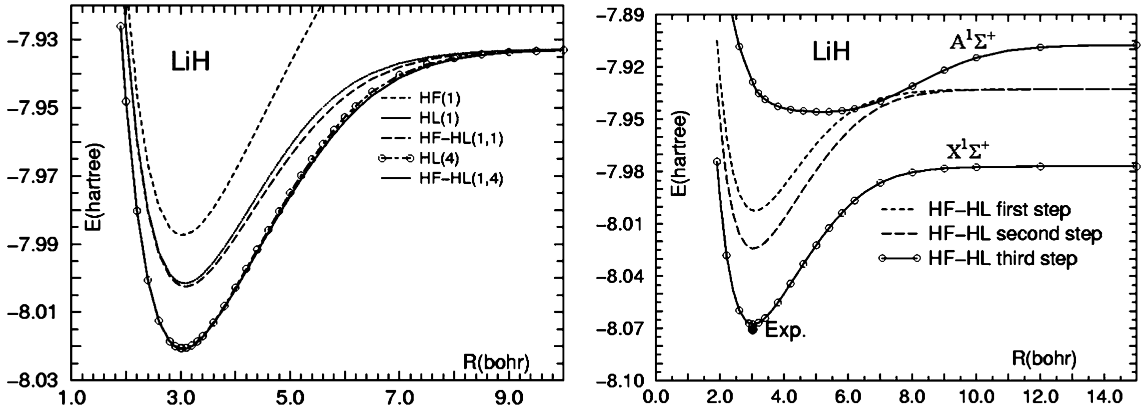

Fig. 6 Potential energies for LiH molecule: in the *left inset* the LiH[$X^1\Sigma^+$] ground state; in the *right inset* the LiH[$X^1\Sigma^+$] and LiH[$A^1\Sigma^+$] states (see text). First, second and third step are Eqs. 14, 16, and 20, respectively

Table 9 Ground and excited state binding energies (kcal/mol) in LiH, and C_2. The energies are from experiments, from HF, from HF–HL Eq. 14, from HF–HL Eq. 16 and from coulomb hole approximation E_b(C–h)

Case	State	E_b(exp)	E_b(HF)	E_b(14)	E_b(16)	E_b(C–h)
LiH	(X) $^1\Sigma^+$	58.00	34.27	43.66	57.32	57.68
	(A) $^1\Sigma^+$	24.82	–	–	–	24.10
C_2	$^1\Sigma_g^+$	147.45	18.27	41.90	127.10	147.44
	$^3\Pi_u$	143.57	72.94	83.72	124.06	145.29
	$^3\Sigma_g^-$	125.91	87.34	100.61	107.30	127.64

(right inset of Fig. 5) we obtain good total energies and the excitation energies remain reasonable, as reported in Table 9. Recalling the importance of near degeneracy in the CH study [42] and considering the data from Fig. 5 and Table 9, we conclude that carbon chemistry is notably influenced by near-degeneracy. The near-degeneracy is important not only for the C_2 molecule but also for Be_2 and B_2.

Let us now summarize the excited state computation for LiH. The LiH[$X^1\Sigma^+$] ground state dissociates into Li[^2S] and H[^2S] and the [$A^1\Sigma^+$] excited state dissociates into in Li[^2P] and H[^2S]. The LiH[$X^1\Sigma^+$] and the [$A^1\Sigma^+$] potential energy curves are reported in the two insets of Fig. 6. The computed curves for the HF, HL and HF–HL(1,1) (designated as “HF–HL first step” in the right inset) show at the equilibrium distance molecular binding energies of 34.27, 43.11 and 43.66 kcal/mol, with total molecular energies of −7.98734, −8.00142 and −8.00230 hartree, respectively. A four configuration optimized MC–HL function (three σ and one π) yields a binding energy of 55.25 kcal/mol; adding the HF component we obtain an HF–HL function with a binding of 57.32 kcal/mol (to be compared with the experimental value of 58.00 kcal/mol) and a total energy of −8.02407 hartree at equilibrium (−7.93272 hartree at dissociation, see in Fig. 6 the curve designated HF–HL(1,4) in the left inset, and designated "HF–HL second step" in the right inset).

A successive computation for partial inner shell correlation, discussed in Ref. [43], yields a binding of 56.83 kcal/mol. The HF–HL–Ch computation yielding a binding energy of 59.22 kcal/mol.

From the MC–HL expansion we obtain also the first excited state curve, given in the right inset of Fig. 6. The computed binding and total energies are 24.10 kcal/mol [see Table 9 as "best computed", (bc), binding, E_b(bc)] and −7.94574 hartree, respectively to be compared with the a "recommended value" by Stwalley et al. [138] of 24.82 kcal/mol. The potential energy has a very flat minimum, with a computed minimum at 5.00 bohr, to be compared with a "recommended value" [144] of 4.91 bohr.

The computed atomic Li [^{2}S] to Li [^{2}P] excitation energy is 0.06797 hartree in excellent agreement with the experimental value of 0.06791 hartree [145].

10 Chemical orbitals

In this section, we propose a new one-electron function, designated the "CO", which, on one hand retains the main characterization of traditional orbitals AO and MO but on the other hand ensures—by construction—a larger variational freedom optimally tuned for different internuclear separations.

The $^1\Sigma_g^+$ ground state for the H_2 molecule is the traditional test for proposals of quantum mechanical models; we display (Fig. 7, left inset) the very accurate, but computationally demanding, potential energy curve obtained by Kołos et al. [109]. The wave function is a 249 term expansion with elliptic type basis set, yielding the accurate binding energy of 109.48 kcal/mol, computed from large internuclear distances to 0.2 bohr. In the figure, to the Kołos et al. landmark computation we add the potential energy computations for the HL, the HF and the HF–HL–i (2), the latter with two ionic structures. In the right insert we display an equivalent representation by reporting both the electronic energy, obtained in the Born–Oppenheimer approximation, and the nuclear–nuclear repulsion. Kołos et al. [109] work is our target in the CO computations below analyzed.

We recall that the long expansions in MC–SCF, CASSCF, MC–HL and VB, and the relative short expansion in the HF–HL model (Eqs. 16–19) is related to the fact that the MO and the AO functions lack sufficient variational freedom, since restricted by "construction constraints", orthogonality, and occupation rules (two electrons for the same space–orbital). These limitations were critically considered last century, starting from the mid fifties, leading to the introduction of new orbital representations aiming at more compact representations. We recall for example the proposals of the Natural Orbitals by Löwdin [122, 123], of the Alternant Orbitals by Pauncz [146], of the non paired spatial orbitals by Linnett [147], of the Electron Propagators by Linderberg [148], Öhrn [148, 149] and Ortiz [150], of the half projected HF functions by Smeyers [151], and of the Geminals, the latter considered also recently by Taylor [152] among others. A survey on "different orbitals for different spins" methods is reviewed by Pauncz [153]; the importance of relaxing the orthogonality constrains has been often documented [154].

Returning to Herzberg [9] and Mulliken [155] orbital correlation diagrams for diatomic molecules, mentioned in Sect. 3, we note that each correlation path is identified by four one-electron functions (occupied either by one or two electrons), specifically two AOs at dissociation, one

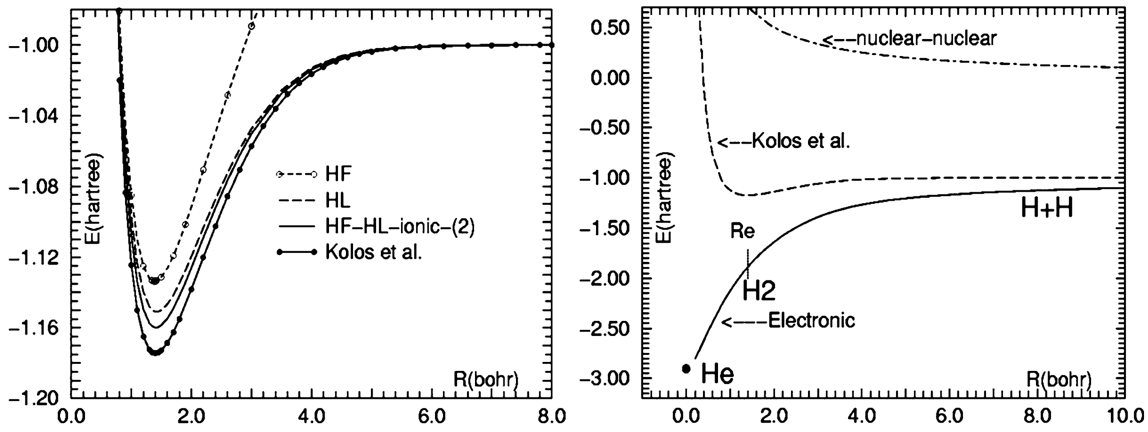

Fig. 7 Potential energy (hartree) for the H_2 ground state. *Left inset* computation with the HF, HL, HF–HL–i(2) models and from Kołos et al. [109]. *Right inset* electronic energy, nuclear–nuclear interaction and total energy from Kołos et al

MO in the intermediate region, and another AO at the united atom, yielding a path valid from dissociation to the united atom.

For each path, occupied with two electrons, i and $i + 1$, we define two new one-electron space functions, called CO, designated u_{i} and $u_{\mathrm{i+1}}$, to which we associate anti-parallel spins yielding the spin–orbitals U_{i} and $U_{\mathrm{i+1}}$. The CO one-electron space function is constructed by a combination of traditional AO-like functions and MO-like traditional functions, both assumed to be linear combinations of basis sets centred at nuclear positions. Neglecting for the moment the united atom, the u_{i} and $u_{\mathrm{i+1}}$ fulfil the point group symmetry requirements of the system and are formed as a linear combination of the above defined MO and AO components. The first component, designated ϕ_{j}, replaces the traditional symmetry adapted MO function, the second component, denoted $\varphi_{\mathrm{k}}(\mathrm{A})$ or $\varphi_{\mathrm{l}}(\mathrm{B})$, replaces the traditional AO functions for an electron on atom A or B, respectively. Thus, we write the two space-components of the CO as:

$$u_i(\gamma_{\mathrm{c}}) = [c_1\Phi_j(\gamma) + c_2\varphi_{\mathrm{k}}(A)]_{\mathrm{i}} \tag{21a}$$

$$u_{i+1}(\gamma_{\mathrm{c}}) = \left[c_1\Phi_j(\gamma) + c_2\varphi_{\mathrm{l}}(B)\right]_{i+1} \tag{21b}$$

where the notation γ_{c} indicates that the CO has the symmetry of ϕ_{j}, the MO-like component, with c_1 and c_2 the variational coefficients. To represent the united atom, ua, we add AO-like functions, denoted $\varphi_{\mathrm{m}}(ua)$, centred midway two nuclei; thus the full expression for $u_{\mathrm{i}}(\gamma_{\mathrm{c}})$ and $u_{\mathrm{i+1}}(\gamma_{\mathrm{c}})$ in a diatomic molecule becomes:

$$u_{\mathrm{i}}(\gamma_{\mathrm{c}}) = \left[c_1\Phi_{\mathrm{j}}(\gamma) + c_2\varphi_{\mathrm{k}}(\mathrm{A}) + c_3\varphi_{\mathrm{m}}(\mathrm{ua})\right]_{\mathrm{i}} \tag{22a}$$

$$u_{i+1}(\gamma_{\mathrm{c}}) = \left[c_1\Phi_j(\gamma) + c_2\varphi_{\mathrm{l}}(\mathrm{B}) + c_3\varphi_m(ua)\right]_{i+1} \tag{22b}$$

When in Eq. 22 the coefficients $c_1 = c_3 = 0$ then the CO reverts to traditional AOs, but when $c_2 = c_3 = 0$ then the CO reverts to traditional MO. This consideration shows that the CO orbital is a generalized representation which includes both the AO and the MO viewpoints.

Consider a n electron diatomic molecule, A–B, which dissociates into the A and B atoms of atomic numbers $Z(A)$ and $Z(B)$, respectively; the united atom for the molecule AB has atomic number $Z(ua) = Z(A) + Z(B)$, and is assumed to be in its lowest electronic state, compatibly with the Wigner and Witmer rules [74]. We consider once more the orbital correlation diagram, specifically a p-path connecting (1) at dissociation the two AOs, $\varphi_{\mathrm{k}}(\mathrm{A})$ and $\varphi_{\mathrm{l}}(\mathrm{B})$, (2) in the binding region the MO ϕ_{j}, and (3) at the united atom, the AO $\varphi_{\mathrm{m}}(ua)$.

In the CO model, to the p-path there correspond two CO spin–orbitals $U_i = u_i\alpha$ and $U_{i+1} = u_{(i+1)}\beta$ with ($i = 1,\ldots, n/2$) and $u_i \neq u_{(i+1)}$ defined as:

$$U_i(\gamma_{\mathrm{c}}) = u_i(\gamma_{\mathrm{c}})\alpha = \left[c_1\Phi_j(\gamma) + c_2\varphi_{\mathrm{k}}(A) + c_3\varphi_m(ua)\right]_i\alpha \tag{23a}$$

$$\begin{aligned} U_{i+1}(\gamma_{\mathrm{c}}) &= u_{i+1}(\gamma_{\mathrm{c}})\beta \\ &= \left[c_1\Phi_j(\gamma) + c_2\varphi_{\mathrm{l}}(B) + c_3\varphi_m(ua)\right]_{i+1}\beta \end{aligned} \tag{23b}$$

with c variational coefficients. In the u_i orbital the MO-like term ϕ_{j}, is combined with the $\varphi_{\mathrm{k}}(A)$, whereas in the $u_{\mathrm{i+1}}$ orbital the same MO-like term is combined to a different AO term, the $\varphi_{\mathrm{l}}(B)$, thus the electrons "maintain a memory" of the original atoms, A and B, yielding different orbitals for different spins. The two CO, (u_{i}) and (u_{i+1}), are normalized and non-orthogonal. With the set of the $U_1,\ldots, U_n$ spin orbitals we construct the Ψ_{CO} wave-function:

$$\Psi_{\mathrm{CO}} = \mathrm{AN}\left[u_1(1)u_2(2)\ldots u_n(n)\Theta^{SM}(1,2,\ldots,n)\right] \tag{24}$$

where A is the anti-symmetrizer operator, N is the normalization constant and $\Theta^{SM}$the spin eigen-functions with the required values of S and M (i.e. a linear combination of spin products). With the CO model we can introduce full correlation correction in the wave functions via variational linear expansion of Ψ_{CO} functions, $\Psi = \Sigma_i c_i \Psi_{\mathrm{CO}}(\mathrm{i})$.

The CO orbital replaces the traditional AO and MO; in Fig. 1 we show wave functions for H_2 obtained in the HF, HL, HF–HL and CO representations.

The CO orbital is selected to represent those electrons we correlate ab initio. Often it is convenient to separate the electrons we wish to compute accurately from those we assume less directly responsible for some molecular property of interest [44], like the binding energy. For example, we might choose to correlate firstly the binding electrons, then the valence electrons and lastly the inner shell electrons. This approach leads to a combined use of different orbitals, CO with MO and/or AO. A wave function with a "mixed representation" of orbitals is designated $\Psi_{\mathrm{CO-HF,}}$ if constructed with COs and MOs, $\Psi_{\mathrm{CO\text{-}HL}}$ if made up of COs and AOs and $\Psi_{\mathrm{CO-HF-HL}}$ if constructed with COs, MOs and AOs. Thus, the set of $\mathrm{u}_1,\ldots,\mathrm{u}_n$ orbitals in Eq. 24 can be partially replaced either by AOs or MOs. For example we can have

$$\Psi_{\mathrm{CO-HF}} = \mathrm{AN}\left[\mathrm{MO}_1(1)\ldots u_n(n)\Theta^{SM}(1,2,\ldots,n)\right] \tag{24a}$$

or

$$\Psi_{\mathrm{CO-HL}} = \mathrm{AN}\left[\mathrm{AO}_1(1)\ldots u_n(n)\Theta^{SM}(1,2,\ldots,n)\right] \tag{24b}$$

Let us consider the ground state of LiH, represented in the HF model by the electronic configuration $1\sigma^2 2\sigma^2$ or in the HL model by the "structure" $1\mathrm{s}_{\mathrm{Li}}^2 2\mathrm{s}_{\mathrm{Li}}^1 1\mathrm{s}_{\mathrm{H}}^1$. The Ψ_{CO} is constructed with the inner shell electrons CO orbitals $u_1(1\sigma_{\mathrm{C)}} = [\mathrm{c}_1 1\sigma + \mathrm{c}_2 1\mathrm{s}_{\mathrm{Li}} + \mathrm{c}_3 1\mathrm{s}_{\mathrm{Be}}]$, and $u_2(1\sigma_{\mathrm{c}}) = [\mathrm{c}_1 1\sigma + \mathrm{c}_2 1s'_{Li} + \mathrm{c}_3 1s_{Be}]$ and, for the valence electrons, with the CO orbitals $u_3(2\sigma_c) = [c_1 2\sigma + c_2 2s_{Li} + c_3 2s_{Be}]$, and $u_4(2\sigma_c) = [c_1 2\sigma + c_2 1s_H + c_3 2s_{Be}]$.

If we wish to correlate only the binding electrons with a $\Psi_{CO\text{–}HF}$ function then we can use the $1\sigma^2$ MO representation for the inner shell electrons and $u_3(\sigma_c)$ and $u_4(\sigma_c)$ for the binding electrons; alternatively in a $\Psi_{CO\text{-}HL}$ function, the inner shell electrons are represented with the $1s^2_{Li}$ AO and $u_3(\sigma_c)$ and $u_4(\sigma_c)$ are used for the binding electrons.

In order to understand the formal relation of Ψ_{CO} to Ψ_{HF}, Ψ_{HL}, and $\Psi_{HF\text{-}HL}$ and to rationalize the presence of ionic structures in homopolar molecules, we decompose Ψ_{CO} into a set of determinantal wave functions of HF and HL type. To simplify the discussion we focus on the Ψ_{CO} for the $H_2[{}^1\Sigma_g^+]$ ground state, denoted $\Psi_{CO}(1\sigma_{g,c})$:

$$\Psi_{CO}\left(1\sigma_{g,c}\right) = \mathrm{AN}\begin{vmatrix} U_1(1)U_2(1) \\ U_1(2)U_2(2) \end{vmatrix} = N(D_1 - D_2) \tag{25a}$$

with

$$D_1 - D_2 = \begin{vmatrix} u_1(1)\alpha(1)u_2(1)\beta(1) \\ u_1(2)\alpha(2)u_2(2)\beta(2) \end{vmatrix} - \begin{vmatrix} u_1(1)\beta(1)u_2(1)\alpha(1) \\ u_1(2)\beta(2)u_2(2)\alpha(2) \end{vmatrix} \tag{25b}$$

Neglecting for the moment the united atom term, we write u_1 and u_2 as:

$$u_1\left(1\sigma_{g,c}\right) = c_1 1\sigma_g + c_2 1s_A \tag{26a}$$

$$u_2\left(1\sigma_{g,c}\right) = c_1 1\sigma_g + c_2 1s_B \tag{26b}$$

The decomposition of the two determinants in Eq. 25 yields a wave function Ψ_{co} of the form:

$$\Psi_{CO} = N\left\{2c_1^2\Psi_{HF} + c_2^2\Psi_{HL} + 2c_1c_2\left[\Psi'_{HL} + \Psi''_{HL}\right]\right\} \tag{27}$$

or, in general, the related variational HF–HL wave function given below

$$\Psi = c'_1\Psi_{HF} + c'_2\Psi_{HL} + c'_3\left[\Psi'_{HL} + \Psi''_{HL}\right] \tag{28}$$

where the c' are variational coefficients and

$$\Psi'_{HL} = A\left|1\sigma_g\alpha 1s_B\beta\right| \quad \Psi''_{HL} = A\left|1s_A\alpha 1\sigma_g\beta\right|$$

A further decomposition of the wave functions containing the $1\sigma_g$ molecular orbital, into Ψ'_{HL} and Ψ''_{HL}, yields a function, designated "adjoined HF–HL function", $\Psi^a_{HF\text{–}HL}$, given below:

$$\Psi^a_{HF-HL} = c'_1\Psi_{HF} + c'_2\Psi_{HL} + c'_3\Psi^*_{HL} + c'_4\Psi^{**}_{HL} + c'_5\Psi_{HL,iA} + c'_6\Psi_{HL,iB} \tag{29}$$

with

$$\Psi_{HF} = A\left|1\sigma_g\alpha 1\sigma_g\beta\right| \quad \Psi_{HL} = A\left|1s_A\alpha 1s_B\beta\right|$$

$$\Psi^*_{HL} = A\left|1s'_A\alpha 1s_B\beta\right| \quad \Psi_{HL,iA} = A\left|1s'_A\alpha 1s_A\beta\right|$$

$$\Psi^{**}_{HL} = A\left|1s_A\alpha 1s'_B\beta\right| \quad \Psi_{HL,iB} = A\left|1s'_B\alpha 1s_B\beta\right|$$

and where the coefficients c'_i are variational parameters (subject to the symmetry constrains, $c'_3 = c'_4$ and $c'_5 = c'_6$). Note that $1s_A$ and $1s_B$ are rather similar to $1s'_A$, and $1s'_B$ and this can lead to redundancy in the solution of Eq. 29. In the above analyses, we have simplified the CO of Eq. 23 by neglecting the united atom term. Clearly, inclusion of the united atom will increase the number of terms in Eq. 29 with functions related to the He atomic ground state; this brings about additional variational flexibility, particularly at short internuclear distances.

We have obtained an important conclusion: the Ψ_{CO} wave function of Eq. 25a is equivalent to specific extended HF–HL–i, which we call the "adjoined HF–HL–CO" function, denoted as Ψ^a_{HF-HL}.

11 Chemical Orbitals for the H_2 molecule

In the following, we compare the Ψ_{HF}, Ψ_{HL}, $\Psi_{HF\text{-}HL}$, $\Psi_{HF\text{-}HL\text{-}i}$ functions with the CO adjoined Ψ^a_{HF-HL} for the H_2 ground state. This comparison advises to revisit the original classical computations with minimal basis sets performed with Slater type orbital, STO, by Heitler and London [8] and by Coulson for the LCAO–MO model [156]. The many-centre integrals with STO are computed with the SMILES set of computer codes [157].

We start with HF and HL wave functions. For the Ψ_{HF} one $1s$ STO, with optimized orbital exponent $\zeta_{HF} = 1.197$ yields $Re = 1.39$ bohr and a binding of 87.27 kcal/mol, confirming the original Coulson computation [156]. For the Ψ_{HL} a $1s$ STO with orbital exponent $\zeta_{HL} = 1.0$ yields a binding of 72.76 kcal/mol reproducing the value of the original Heitler–London computation [8]; optimization of the $1s$ orbital exponent leads to $\zeta_{HL} = 1.1670$ and a binding of 87.27 kcal/mol at $Re = 1.41$ bohr.

A computation of $\Psi_{HF\text{–}HL}$ with one $1s$ STO optimized at each internuclear separation, yields $\zeta_{HF\text{–}HL} = 1.194$ at $Re = 1.43$ bohr, with a biding of 92.83 kcal/mol. This basis set could be considered "sub-minimal", since we have used the same orbital exponent for the $1s$ STO in HF and HL models, whereas a minimal basis set for $\Psi_{HF\text{–}HL}$ would call for distinct values for ζ_{HF} and ζ_{HL}. However, optimization of these two parameters yields $\zeta_{HF} = 1.194$, $\zeta_{HL} = 1.194$ for $Re = 1.43$ and a binding of 92.83 kcal/mol; indeed full expansions of both models leads to the same energy, as discussed by Coulson.

A minimal basis set computation for $\Psi_{HF\text{–}HL\text{–}i}$ with optimal parameters yields $\zeta_{HF} = 1.1878$, $\zeta_{HL} = 1.1647$, $\zeta_{H-} = 1.2050$ for $Re = 1.42$ and a binding of 94.62 kcal/mol; this energy improvement follows the increased flexibility introduced by augmenting the basis set, the ionic $1s$ function in our case.

A "sub-minimal" basis set for the Ψ^{a}_{HF-HL} model, Eq. 29, makes use of one $1s$ STO for the H atom (assuming $\zeta_{HF} = \zeta_{HL} = \zeta_{H}-$) and one $1s$ STO for He [$^{1}S(1s^{2})$], the united atom. The 1 s orbital exponent for the H atom, optimized at each internuclear separation, is $\zeta_{H} = 1.180$ at $Re = 1.42$ bohr; for the He united atom we use $\zeta_{He} = 1.6875$, the atomic minimal basis set value for He(^{1}S) (yielding an atomic energy of -2.84766 hartree [85]); with these two 1s functions the computed binding is 96.05 kcal/mol. A minimal basis set Ψ^{a}_{HF-HL} computation with distinct ζ_{HF}, ζ_{HL}, and ζ_{H}—taken, however, from the previous $\Psi_{HF-HL-i}$ computation and an optimized value for ζ_{He} yields, at $Re = 1.42$, $\zeta_{He} = 1.349$ and a binding of 98.51 kcal/mol. Finally, simultaneous re-optimization, at $Re = 1.42$, of all the orbital exponents, ζ_{HF}, ζ_{HL}, $\zeta_{H}-$, and ζ_{He}, yields a Ψ^{a}_{HF-HL} with a binding of 98.55 kcal/mol and $\zeta_{HF} = 1.18697$, $\zeta_{HL} = 1.16702$, $\zeta_{H}- = 1.20748$, and $\zeta_{He} = 1.3100$. This concludes our analysis of minimal basis set STO computations; previously [1, 44] we have reported only a partial set of the computations with minimal STO basis sets.

Additional improvements, but maintaining the constraint of minimal basis sets, can be obtained by configuration interactions. For example, addition of one $\Psi^{a}_{HF-HL}(\pi^{2}_{u})$ configuration with $\zeta_{HF} = 1.1716$, $\zeta_{HL} = 1.1649$, $\zeta_{H}- = 1.2075$, and $\zeta_{He} = 1.3075$, $\zeta_{\pi,HF} = \zeta_{\ \pi,HL} = 2.065$, and $\zeta_{He,2p} = 1.512$ yields a binding energy of 106.02 kcal/mol and $Re = 1.40$. This last computed binding energy can be compared with the excellent work by McLean et al. [158]: a basis set of five optimized STO ($1s$,$1s'$, $2s$, $2p_{\sigma}$, $2p_{\pi}$) and ten CI configurations, yields a binding of 104.96 kcal/mol.

The potential energies for these computations are reported in Fig. 8; in Table 10 we report the STO orbital exponents, the binding energy, the computed equilibrium separation, and the corresponding experimental values. At the STO minimal basis set level, the best computed energies using different "one electron functions" are in the following order: first the Ψ^{a}_{HF-HL} (98.55 kcal/mol), followed by $\Psi_{HF-HL-i}$ (94.62 kcal/mol), Ψ_{HF-HL} (92.47 kcal/mol) then by Ψ_{HL} (87.27 kcal/mol) and finally by Ψ_{HF} (80.45 kcal/mol).

The energy improvements are related to an increased dimensionality of the variational space (with the full CI as its limit) either due to an increase in the number of basis functions, or to a decrease in the constrains implicit in the adopted one electron function, AO, MO, or CO. The MO has the constrain of its ionic component, the CO has the same constraint but is more flexible than the MO because of the added function at the united atom. Indeed, in H_2, comparing HF and HL, the results in Table 10 show a better value for HL since the HL wave function is composed by two determinants rather than one, as in the HF wave function. The HF–HL wave function is composed by three determinants, thus is expected to yield a better energy relative to HF or HL alone. Notice that when only one basis function is used, the HF full CI energy (the wavefunction is composed by two configurations, gerade and ungerade), coincides with the HL full CI energy (with wavefunction composed by three configurations, one covalent and two ionic); the same energy value is obtained by combining the HF gerade configuration with the covalent HL configuration, i.e. the HF–HL wavefunction.

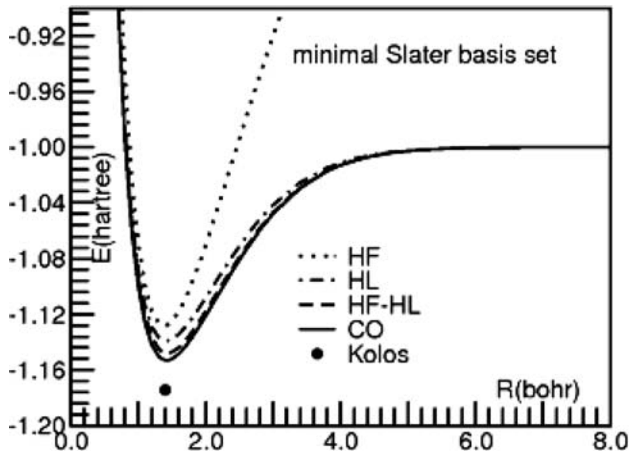

Fig. 8 *Single configuration* STO computations minimal basis set for H_2. Potential energy curves from HF, HL, HF–HL, and CO methods

These computational results characterize the evolution in classical one-electron function representations with variational quantum chemical computations since 1927.

We have experimented with a more extended basis set of Slater type functions, specifically six $1s$, one $2s$, six $2p$, four $3d$, and one 4f functions on the H atoms with a four $1s$, two $2s$, three $2p$ Slater type functions on the united atom; the Ψ^{a}_{HF-HL} binding and total energies are 108.72 kcal/mol and -1.17314 hartree, respectively, with a multi-configuration of three σ, two π and two δ configurations (see Table 10).

Let us consider computations with an extended basis sets of gaussian type functions. For the H atom we use a basis set of gaussian functions, with ten 1 s, five 2p, four 3d functions and one 4f gaussian function, contracted to 6,5,4,1 functions, respectively. This is a reasonably accurate basis set, yielding a full CI binding of 109.09 kcal/mol and a total energy of -1.17384 hartree. In these computations we have included the He united atom component, computed with a basis set yielding the correct Hartree–Fock total energy of -2.861679 hartree for the He(^{1}S) [83] and -2.90089 hartree from a full CI computation, a value near to -2.90372 hartree, the exact non relativistic energy [159].

We recall that the single configuration $\Psi_{CO}[1\sigma^{2}_{g,c}]$ is not expected to yield a fully correlated wave function, since the

Table 10 H_2 ground state computations of the binding energy E_b (kcal/mol) at the computed equilibrium internuclear distance *Re* (bohr) with minimal (min.) STO basis sets for different models: Ψ_{HF}, Ψ_{HL}, $\Psi_{HF\text{–}HL}$, $\Psi_{HF\text{–}HL\text{–}i}$, and $\Psi^a_{HF\text{–}HL}$from Ψ_{CO} of 1 and 2 and 7 configurations

Config.	Model	STO orbital exponents	E_b, kcal/mol	*Re*, bohr
σ_g^2	Ψ_{HF} (min.)	$\zeta_{HF} = 1.1872$	80.45	1.39
σ_g^2	Ψ_{HL} (min.)	$\zeta_{HL} = 1.1670$	87.27	1.41
σ_g^2	$\Psi_{HF\text{–}HL}$ (min.)	$\zeta_{HF\text{–}HL} = 1.194$	92.83	1.43
σ_g^2	$\Psi_{HF\text{–}HL\text{–}i}$ (min.)	$\zeta_{HF} = 1.1878$, $\zeta_{HL} = 1.1677$, $\zeta_{H-} = 1.2050$	94.62	1.43
σ_g^2	$\Psi^a_{HF\text{–}HL}$(min)	$\zeta_{HF} = \zeta_{HL} = \zeta_{H-} = 1.189$, $\zeta_{He} = 1.6875$	96.05	1.42
σ_g^2	$\Psi^a_{HF\text{–}HL}$(min.)	$\zeta_{HF} = 1.188697$, $\zeta_{HL} = 1.16702$ $\zeta_{H-} = 1.2074$, $\zeta_{He} = 1.3100$	98.55	1.42
$\sigma_g^2 + \Pi_u^2$	$\Psi^a_{HF\text{–}HL}$(min.)	$\zeta_{HF} = 1.1716$, $\zeta_{HL} = 1.1649$, $\zeta_{H-} = 1.2075$, $\zeta_{He} = 1.3075$ $\zeta_{\pi,HF} = \zeta_{\pi HL} = 2.065$, $\zeta_{\pi He} = 1.512$	106.02	1.40
Seven conf.[a]	$\Psi^a_{HF\text{–}HL}$	(Extended basis set; see text)	108.72	1.40
	Kołos et al.[b]		109.48	1.40

[a] With seven configurations: three σ, two π, two δ

[b] Ref. [109]

Table 11 H_2 and LiH ground state energies with extended approximately optimal, gaussian basis sets. *Top* for H_2: number of CI terms in Ψ_{CO} wave function expansion, electronic energies (hartree), $E_{el}(R = 0)$, $E_{el}(R = 0.1)$ at $R = 0$ and $R = 0.1$ bohr, total energy (hartree) at $R = Re = 01.40$, $E_{Tot}(Re)$, binding energies (kcal/mol) at $R = 1.40$ bohr, E_b. *Bottom* for LiH: Equilibrium total energies (hartree), $E_{Tot}(Re)$, and binding energies (kcal/mol), E_b, with and without Be united atom component

H_2[a]	CI # terms	E_{el} $(R = 0)$	$E_{el}(R = 0.1)$	$E_{Tot}(Re)$	E_b
Ψ(I)	1	–2.86168	–2.85352	−1.15946	100.07
Ψ(II)	2	−2.877999	−2.85486	−1.16039	100.65
Ψ(III)	3	−2.89707	−2.86830	−1.17190	107.87
Ψ(IV)	4	−2.89810	−2.86873	−1.17227	108.10
Ψ(XI)	11	−2.89985	−2.87020	−1.17358	108.92
Full CI[b]	1,078	–	–	−1.17384	109.09

LiH	E_{Tot} (*Re*) without Be	E_{Tot} (*Re*) with Be	E_b without Be	E_b with Be
$\Psi_{HF\text{–}HL}$	−8.00230	n. a.[b]	43.66	n. a.[b]
$\Psi_{HF\text{–}HL\text{–}i}$	−8.00699	n. a.[b]	46.59	n. a.[b]
$\Psi_{CO\text{–}HF}$	−8.00365[c]	−8.01506[c]	44.51	51.67
Ψ(I)	−8.02327	−8.02950	43.79	47.69
Ψ(II)	−8.05455	−8.05873	53.75	56.38

[a] H_2 exact n.r. binding 109.485 kcal/mol

[b] Not-applicable due to method construction

[c] With $1\sigma^2$ frozen to the $1\sigma^2$ HF orbital

latter requires linear combination of $\Psi_{CO}[1\sigma^2_{g,c}]$with configurations of different symmetry, and/or higher excitations, like $\Psi_{CO}[2\sigma^2_{g,c}]$, $\Psi_{CO}[1\pi^2_{u,c}]$, $\Psi_{CO}[1\sigma^2_{g,c}]$, etc… For each one of the aboveΨ_{CO}functions there is an adjoined HF–HL–CO function, denoted $\Psi^a_{HF-HL}[1\sigma^2_{g,c}]$, $\Psi^a_{HF-HL}[2\sigma^2_{g,c}]$, $\Psi^a_{HF-HL}[1\pi^2_{u,c}]$and $\Psi^a_{HF-HL}[1\pi^2_{g,c}]$, respectively.

We consider four different configuration expansions, Ψ(I), Ψ(II) Ψ(III) Ψ(IV) adjoined functions, specifically:

$$\Psi(\mathrm{I}) = \Psi_{CO}\left[1\sigma^2_{g,c}\right]$$

$$\Psi(\mathrm{II}) = c_1\Psi(\mathrm{I}) + c_2\Psi_{CO}\left[2\sigma^2_{g,c}\right]$$

$$\Psi(\mathrm{III}) = c_1\Psi(\mathrm{II}) + c_2\Psi_{CO}\left[1\pi^2_{u,c}\right]$$

$$\Psi(\mathrm{IV}) = c_1\Psi(\mathrm{III}) + c_2\Psi_{CO}\left[1\pi^2_{g,c}\right]$$

The computational results are summarized in Table 11 and partly displayed in Fig. 9. Details are reported in Ref. [44].

The Ψ(I) wave function at $R = 1.40$ bohr yields the electronic energy of −1.87375 hartree with a binding of 100.07 kcal/mol. At $R = 0$ the electronic energy is −2.86168 hartree, namely the He Hartree–Fock energy. The computation of Ψ(II), yields binding energies of

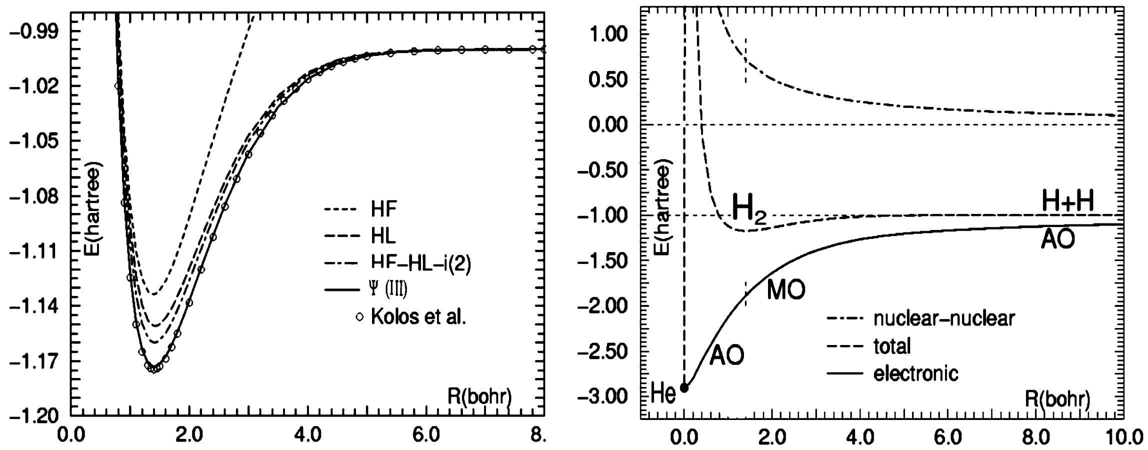

Fig. 9 H_2 ground state. *Left inset* ground state potential energy curves with extended gaussian basis set from HF, HL, HF–HL–i(2), Ψ(III), Kołos et al. [109]. *Right inset*: Ψ(III) computed energies from Ψ_{CO} model from He(^1S) at $R0 = 0$ to dissociation [two H(^2S) atoms]

100.65 kcal/mol. At $R = 0$ the electronic energy is -2.87799 hartree, thus the united atom starts to be correlated. Computation of Ψ(III), yields binding energies of 107.87 kcal/mol; at $R = 0$ the electronic energy is -2.89810 hartree, not far from the exact value [159] of -2.90372 hartree for He. The computations of Ψ(IV) show no appreciable improvement in the binding energies, 108.10 kcal/mol, indicating that the linear expansion with this basis set has essentially converged at Ψ(IV).

The binding energy from Ψ(IV) is not far from the value 108.56 kcal/mol obtained with the HF–HL method and a 22 term expansion. An 11 configuration expansion, Ψ(XI), yields a total energies of -1.17358 hartree, and a binding energy of 108.92 kcal/mol. With this computation we feel that the convergence of the Ψ_{CO} expansion is essentially reached with this Gaussian basis set.

To approach more closely the energy values obtained by Kołos et al. [109] the basis set should include functions with more accurately optimized orbital exponents and of higher angular momentum; however, this requires more and more computer time. Indeed, a somewhat larger Gaussian basis set (addition of three 4f and one 5g functions) for a seven configurations wave function yields a binding of 109.01 kcal/mol. Alternatively, with a somewhat larger basis set of STO functions (relatively to the one previously discussed) namely by adding a 5g STO, the computed total and binding energies are -1.174302 hartree and 109.33 kcal/mol, respectively; equivalently, with an improved Gaussian function basis set (with 6 h functions) the computed energies are -1.174382 hartree and 109.43 kcal/mol (work in progress) not far from the exact value 109.47 kcal/mol. It seems clear that Kolos value will be duplicated for example with a gaussian basis set including up to “l” functions and about a dozen of configurations.

In Fig. 9, left inset, we report the potential energy curves for the HF, HL, HF–HL–i(2), and Ψ(III) wave function functions. In the right inset we report the computed potential energy curves for Ψ_{CO}(III) and the corresponding nuclear–nuclear repulsion and electronic energy from united atom to dissociation. In this inset we indicate the internuclear regions where the three orbital components—AO for the united atom, MO for the molecule and AO for the dissociated atoms—are dominant in the CO representation.

In Fig. 1 we have compared the wave functions for the HF, HL, HF–HL method, and with Ψ(XI), designated CO(I). The “different orbital for different spins” character of the CO is evident from the figure.

Above we have compute the electronic energy of H_2 from dissociation—two H (^{2}S) atoms—to He(^{1}S), the united atom. In the same way that we have formed He, by approaching a H atom to a target atom (the second H atom in the case of H_2), we can compute the electronic energy of any atom A(Z)—with atomic number Z—by approaching a H atom to the atom A(Z–1), where the atom A(Z) is the united atom of the process. Thus, a sequential set of this type of computations is capable to construct ab initio the entire periodic table of the elements, simply by starting with hydrogen atoms colliding with an atom, which is the united atoms computed in the previous computation. In short, we need only H atoms to build the entire set of atoms of the periodic table. Clearly the above sequential processes needs—at the end of each step—inclusion from a suitable source of the appropriate number sub-nuclear particles (e.g. the neutrons) to yield stable nuclear structures, conforming to laboratory observations; this, however, is not a concern in Born–Oppenheimer computations.

12 Chemical orbitals computation for the LiH molecule

In molecules with many electrons the computation of the “adjoined HF–HL” function $\Psi^{a}_{\text{HF–HL}}$ implies a rather heavy computational task, since to each CO there corresponds a large set of decomposition terms (see Eq. 29). For this reason, considering LiH, we have introduced the simpler $\Psi_{\text{CO–HF}}$ type function and $\Psi_{\text{CO–HL}}$ type function functions (Eqs. 24b, c) the first one, $\Psi_{\text{CO–HF}}$, with the two COs for the binding electrons, and the traditional MO $1\sigma^2$ for the inner shell and the second function, $\Psi_{\text{CO–HL}}$, again with two COs for the binding electrons but the traditional AO $1s^2_{\text{Li}}$ for the inner shell.

We first report on $\Psi_{\text{CO–HF}}$ and $\Psi_{\text{CO–HL}}$ and then on a full Ψ_{CO}; the gaussian basis set adopted is the one reported in Sect. 4.

The electronic configuration for $\Psi_{\text{CO–HF}}$ is $1\sigma^2$ $u_3(2\sigma_c)u^1{}_4(2\sigma_c)^1$; its computation without the Be united atom term, yields a binding energy of 44.51 kcal/mol and a total energy of −8.00365 hartree. The computation of $\Psi_{\text{CO–HL}}$ with configuration $1s^2_{\text{Li}}u_3(2\sigma_c)^1u_4(2\sigma_c)^1$, also without the Be united atom, yields essentially the same binding energy and total energies, since the HF and HL core are very similar. Inclusion of the united atom, $\text{Be}[^1\text{S}(1\text{s}^2 2\ \text{s}^2)]$ and $\text{Be}[^1\text{S}(1\text{s}^2 2\text{p}^2)]$, brings the computed binding energy to 51.67 kcal/mol, and the total energy to −8.01506 hartree.

For Ψ_{CO} we present two computations: the first Ψ(I) is a one configuration Ψ_{CO} function with configuration $u_1(1\sigma_c)^1u_2(1\sigma_c)^1u_3(2\sigma_c)^1u_4(\sigma_c)^1)$, the second Ψ(II) is a linear combination of three Ψ_{CO} functions, namely Ψ(I) to which we have added two new configurations $u_1(1\sigma_c)^1$ $u_2(1\sigma_c)^1u_3(1\pi)^1u_4(1\pi)^1)$ and $u_1(1\sigma_c)^1u_2(1\sigma_c)^1u_3(1p_\sigma)^1$ $u_4(1p_\sigma)^1)$ with $2p_\pi$ and $2p_\sigma$ functions on the Li and H atoms (see Table 11).

The Ψ(I), without the Be united atom, yields a binding energy of 43.79 kcal/mol and a total energy of −8.02327 hartree; inclusion of the Be united atom yields a binding energy of 47.69 kcal/mol and a total energy of −8.02950 hartree.

Next we improve the binding with Ψ(II). Without the Be united atom component it yields a binding energy of 53.75 kcal/mol and a total energy of −8.05445 hartree; the full computation with the Be united atom yields a binding of 56.38 kcal/mol and a total energy of −8.05873. The computed total energy at dissociation is −7.96889 hartree not far from the exact non-relativistic energy value [134] of −7.97806 hartree. From this study we can conclude that the $\Psi_{\text{CO–HF}}$ and the $\Psi_{\text{CO–HL}}$ represent a useful simplification to the computation of Ψ_{CO}.

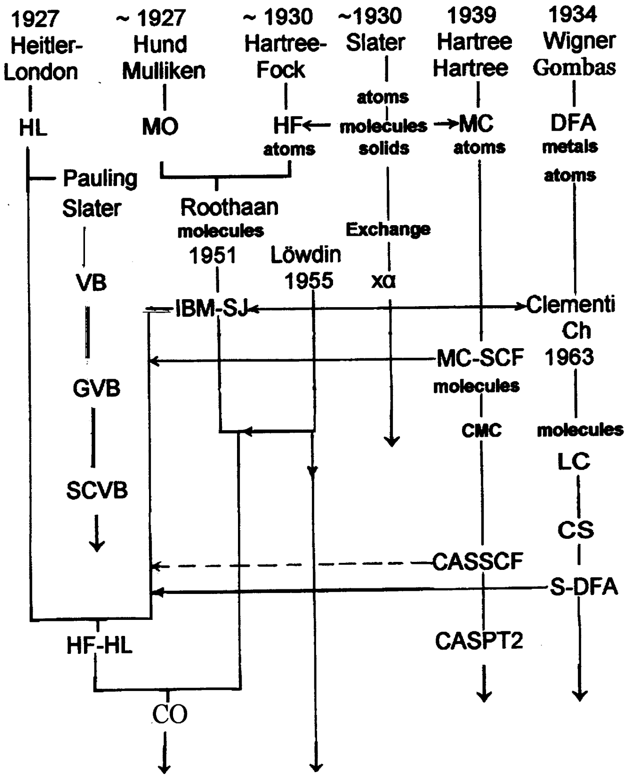

Fig. 10 Genealogy of the HF–HL and of the Chemical orbitals methods

13 Genealogy of the HF–HL method

There are—by now—many approaches in quantum chemistry; therefore, for a new method it is informative to attempt to draw its genealogical tree.

In Fig. 10 we present the genealogical tree for the HF–HL and the CO methods, staring from the beginning of quantum chemistry. Note that each method has it own genealogical tree, and a full representation of all the methods would bring about not a single tree but … a forest. Recognizing that the physical length of the printed page limits the number of entries, we beg the indulgence of the reader for omissions.

We are interested in the origins of the HF–HL and of the Chemical Orbital methods, given on the bottom of the figure; thus we cover in the figure the developments from the late 1920s to the first decade of this century.

At the top we list a few names relevant to the HF–HL method for their seminal proposals. This first line needs no comment; it remind us, however, that very little is conceptually new—in a rigorous sense of the word—in today computational chemistry: the concepts birth-dates are around the early 1930, the computer implementations start in the early 1960s, followed by continuous improvements, keeping up with the computer industry progress and the expanding interest of chemistry into pharmacology, new materials, medicine and ecology, etc.

The HF–HL method has clearly its roots both in the HL and in Roothaan's RHF methods. This neglects the techniques needed to deal with the correlation effects. Basic to our treatment of the correlation energy is the realization that the correction is not dependent from a single source but from several; thus the decomposition into near-degeneracy effects, molecular extra correlation, and atomic correlation. All this leads in the genealogical three to a link from Clementi's work in IBM San Jose, [92, 160] to the HF–HL and the CO models. Finally, the use of DFA, the Coulomb Hole approximation in particular, requires a link to DFA's line of development, initiated by Wigner. We recall in this contest that the Lie and Clementi functional (designated in the figure as "LC") and the Colle–Salvetti functional [140] (designated as "CS") are the earliest attempts to use density functional for Multi configuration functions. The use of multi configurations, particularly MC–HL, in the HF–HL method calls for a link to the Multi Configuration line of development, with Hartree at its origin, but the use of non-orthogonal orbitals calls particularly for a link to Löwdin and to the Uppsala international school started in the mid ninety fifty [121, 122, 146–154], denoted simply as "Löwdin" in Fig. 10. Since parallel to the DFA approach there is the Slater xα formulation, the latter is included in Fig. 10, as a step of importance.

14 Conclusions

We have considered a few logically and formally related models proposed to describe the electronic structure of molecules within the variational approach.

Two traditional quantum chemical molecular methods, HF and HL, were advanced in the early 1930; both underestimate the total energy by a large percentual error in the binding energy, and the HF model yields incorrect dissociation.

The HF–HL model recently proposed (1) provides a method for variational ab initio computations of the molecular extra correlation energy, leading to very realistic computations of the binding energies obtained with relatively *short linear* expansions, (2) even at its simplest level (Eq. 16) the HF–HL model constitutes a reliable "zero-order reference wave function" with correct dissociation and qualitative correct binding, (3) with the Coulomb hole density functional it allows to easily obtain realistic total energy (4) both for ground and excited states, and (5) it demonstrates the clear complementarities of HF and HL methods, replacing incorrect assumptions of antagonisms.

The HF–HL method is based on the combination of two traditional orbitals, MO and AO, thus it requires two models, the HF and the HL, and a set of pragmatic rules proposed to select the HF configurations and HL structures. This somewhat redundant situation has evolved with the introduction of the CO, which retains the characteristic of both the traditional MO and AO orbitals, adds variational flexibility and uses only one type of one electron functions. Thus the CO is a new, flexible and very compact one-electron function, which provides the logical origin of the HF and VB methods, and brings to a conclusion the evolution of the two classical variational methods. This evolution path logically starts with Ψ_{CO} then it progresses to $\Psi^{a}_{\mathrm{HF-HL}}$ and subsequently to $\Psi_{\mathrm{HF-HL}}$; here it bifurcates into two avenues the first one is the Ψ_{HF} method, with subsequently FCI, MC–SCF, CSSCF, CASSPT2 techniques and the second avenue is given by Ψ_{HL} method with subsequently the different VB implementations. Realistic binding energies can be obtained either at the start ($\Psi^{\mathrm{a}}_{\mathrm{HF-HL}}$ and $\Psi_{\mathrm{HF-HL}}$) with relatively short expansions or at the end (FCI and CASSPT2) with very long expansions.

We conclude that in theoretical chemistry much progress has been made since its beginning 1980 to 1990 years ago; this is true also for computational chemistry.

The traditional "chemical bond" is a partial and localized representation extracted from model equations which only mimics the nature of a "molecule" still often considered at zero temperature and in vacuo. But the concept of "chemical bond" remains most useful to those interested in building up or in breaking molecules in a laboratory or in an industrial assembly line, at finite temperatures and not in vacuo. The outstanding intuition and creativity of laboratory chemists and biochemists appear to be able to compensate theoretical limitations; indeed, chemistry is not reducible to quantum mechanics.

Recalling [1–3] the apeiron of Tales, the atom of Democritus, the rituals of the alchemy time, the hypotheses on phlogiston, caloric, chemical affinity, vital force, the atom of Dalton, the atom of Bohr, the Lewis-pair, the semi-empirical models, the evolving concepts of one-electron function from Atomic, Molecular, and Chemical Orbitals, as well all the ab initio quantum chemistry representation of today theoretical and computational chemistry, we witness a many centuries evolution more and more based on physical concepts; but we are still at an early stage in the search for an satisfactory representation of a model of the chemical bond with " reliable bond transferability, molecule to molecule" within a realistic environment.

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