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REGULAR ARTICLE

Merging two traditional methods: the Hartree–Fock and the Heitler–London and adding density functional correlation corrections

Enrico Clementi · Giorgina Corongiu

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Abstract The variational combination of the Hartree–Fock (HF) with the Heitler–London (HL) methods, yielding the Hartree–Fock–Heitler–London (HF–HL) method is analyzed for diatomic hydrides and homonuclear molecules of the first and second row atoms. This recent quantum chemistry development is considered in the light of the continuous evolution of hypotheses and corresponding verifications occurring in quantum chemistry. The correlation energy correction needed in HF and HL computations is reduced in the HF–HL method to its dynamic component, since the non-dynamical correlation is accounted by explicitly considering near degeneracy and state crossing. The dynamical correlation is computed either (1) via expansion with multi-configuration of HF and HL functions or (2) including ionic HL structures, yielding a large fraction of the molecular extra correlation energy or (3) using the Coulomb hole density functional. With the latter the computed total and binding energies for all internuclear separations are in excellent agreement with laboratory data.

Keywords Serafin Fraga · Hartree–Fock · Heitler–London · HF–HL · Diatomic hydrides · Diatomic homopolar · Non-dynamical correlation · Dynamical correlation · Avoided crossing · Reference wavefunction · Density functional approximation · DFA · Coulomb hole functional

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Contribution to the Serafin Fraga Memorial Issue.

E. Clementi (✉)
Via Carloni 38, 22100 Como, Italy
e-mail: clementi@fis.unico.it

G. Corongiu
Dipartimento di Scienze Chimiche ed Ambientali,
Università dell'Insubria, Via Lucini 3, 22100 Como, Italy

0 Foreword

The molecular orbital (MO) and the Heitler–London (HL) approximations constitute the two pillars on which the development and construction of today quantum chemistry is based. The late Prof. Serafin Fraga was well aware that both methods are valid tools to explain molecular binding. About one half century ago, in his paper with Mulliken, Serafin Fraga [1] did analyze the Heitler–London approach considering the role of the coulomb energy and advocating a modified Heitler–London as to include a promotional energy contribution term, approximately the equivalent of today polarization function effects in the HF model. In their conclusions, Fraga and Mulliken, realizing the algebraic and numerical complexity of their suggestion, returned on a previous work by Mulliken [2] by proposing a pragmatic and phenomenological solution, by them candidly designated as a *"magic formula"*, namely, an approach, we today dignify as *"semi-empirical approach"*.

In this paper, we return on Fraga's steps with an analysis of the two basic methods, but realizing the unique contribution of the two different physical hypotheses at different internuclear distances, we have decided to keep them both and simply merge the two models into one. Indeed, the underlining assumption of the HF method is that molecules are built by nuclei and electrons, whereas the HL method assumes that molecules are built by combining atoms. Clearly, both assumptions are valid to a first approximation; HF is the model of choice from the united atom to equilibrium separations, but HL is obviously the correct model at molecular dissociation. By construction the electrons, the objects of motion represented with the Schrödinger equation, either envelop the entire nuclear system or specific nuclei of the atoms constituting the molecule; in both cases the constraints and the limitations imposed by the Born–Oppenheimer [3] approximation are maintained.

We all know that the HF approximation for molecular computations is indelibly related to the research carried out for three to four decades at the Laboratory of Molecular Structure and Spectra, LMSS, Department of Physics, at the University of Chicago, Chicago, IL, USA.

In the very late 1950 and early 1960, Serafin Fraga was one among the theoreticians at LMSS; others among the visiting scientists and the students were W. Kołos, R. A. Sack, B. J. Ransil, S. Huzinaga, P. E. Phillipson, R. Moccia, one of us (E.C.) and among the young students we recall A. W. Weiss, A. D. Mc Lean, M. Yoshimine and—but later—G. Malli, P. Bagus, G. C. Lie and B. Liu. The laboratory experimental researchers, the spectroscopists, also had an office in the Ryerson building at the University, but downstairs, near the instruments; the theoreticians, were crowded upstairs in the third floor with Mulliken, Roothaan and the LMSS secretary.

It was a time of creative excitement, hard work, sharing of ideas, good relations and friendship. It was clear to all of us at LMSS that we were creating the base for a new chemistry with a new tool, the computer, but it was not evident how to improve on the LCAO—MO approximation, even in the new form proposed by Roothaan, the restricted Hartree–Fock approach. Eventually, the decision favored the abandoning of the CI approach in favor of extended MC–SCF expansions.

At the time there were no computers in the Chicago area; therefore, very frequently one would fly to Dayton in Ohio to use the computational facilities at the Wright Field Development Center, a USA Air Force base. The nearly weekly trips, often with overnight stay in Dayton (on a rather limited budget from the University of Chicago) did reinforce the already strong comradeship spirit.

Most of the postdoctoral did arrive to Chicago from different Countries and the today nearly universal use of the English language was at that time a restricted commodity; indeed, many among us learned English on quantum chemistry books and journals, with limited attention to conversational English.

Dr. A. D. McLean reminded us of the following anecdote. Serafin did not show up to the laboratory as expected on the next day after his arrival from Spain (an early day in the week); therefore, the LMSS people were concerned, and contacted him by telephone. Serafin answer was very slow in coming and limited to the sentence “I will be in Monday”: in the hotel Serafin was busy attempting to learn English in less than 1 week and practicing conversation by listening as many Western movies as he could. The following Monday Serafin finally did show up in the laboratory, his English with a cowboy flavor. According to McLean, Andy Weiss spoke too fast for Serafin, who would employ Kołos as a translator from Andy’s English to Kołos English to Serafin.

The LMSS researchers had well understood the decisive influence of computer technology in the development of theoretical chemistry. This essential connection today is taken for granted, not at that time; we recall that many scientists did look at what today is called “computational chemistry” as a childish enthusiasm, likely of no lasting relevance to chemistry. Equally underestimated by today scientists is the large effort from a minority determined to secure computer hardware and software capable of performing scientific computations rather than only data analyses, graphics and other market or business-oriented activities. It must be admitted in this contest that the battle for scientific computer development most likely would have been lost or delayed without the determining worldwide support from departments of defense. It is indicative in this regard that LMSS scientists would fly to the Wright Field Development Center, not to some scientific center.

Eventually, each visitor departed from LMSS along different roads both geographically and in science. I (E.C.) recall Serafin’s letters letting me know about his difficult adaptation to the winters in Alberta, Canada, the several encounters at international meetings, where Gina and I had the pleasure to see again Serafin and Ester; till the last time in Caceres, in his beloved Spain.

To the memory of Prof. Dr. Serafin Fraga, our good friend, a scientist with a deep and personal vision and a man of great humanity, we dedicate this work.

1 Introduction

1.1 A bit of history

It is well known that, at the beginning of quantum chemistry, two approaches were predominant in the attempt to explain, with quantum theory, the forces responsible for holding atoms together in a molecule. These were the linear combination of atomic orbitals–molecular orbitals [4–6] (LCAO–MO) and the Heitler–London [7] (HL) approximations. These approaches represent two different approximations to the exact one-particle model and did in time evolve into the analytical Hartree–Fock (HF) approximation [8,9] (at the time the HF was a most promising and well tested method for atomic systems [10–12]) and the Valence Bond (VB) approximation [13–18].

Since the LCAO–MO and the HL provide —in general— qualitatively reasonable, but sometimes also notably poor approximations, the last five decades have witnessed a strong effort aimed at providing more accurate quantum mechanical solutions [19,20] often with the two original approximations as a starting point. Among the early improvements we recall the SCF technique adapted to more than one configuration, the multi-configuration SCF approximation [12] eventually leading to the complete multi-configuration SCF approximation [21] and later to the CASSCF computer codes [22,23]. These methods can be considered as "improved technological approaches" relative to the configuration interaction (CI) method [24].

A general way to correct HF-type functions was proposed in the early 1930 by Wigner [25], with a functional of the electronic density parameterized from solutions of the free electron model. Wigner considered the correlation energy as a correction to be estimated once the HF-type density was available. This view was followed and extended particularly in Europe as documented in Gombas volumes [26,27] and papers [28,29].

Later, in the early days of the computer development of quantum chemistry, Clementi [30] modified the Coulomb energy in the HF-self consistent field with a correction term applied directly to the HF–SCF model. 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 [25] "correlation energy". Clementi's correction term essentially introduced a Coulomb hole around two interacting electrons, modifying Wigner main idea. This modified HF solution is the "Clementi orbital and determinant". The correction and extensive applications to atomic HF functions were reported in a review paper [30], at the conclusion of a massive tabulation of atomic HF wavefunctions [31]. The correlation energy for neutral atoms ground and excited states of the lowest configuration and for the corresponding isoelectronic series was thus analyzed and quantitatively explained [32–34] for the first time. Later, Clementi alternated the use of the Coulomb hole with Wigner–Gombas-type density functionals. To extend the concept to molecular systems it was first of all necessary to write a new and general molecular computer code [35,36], several times improved and adapted to computer hardware evolution. This post-HF approach is indicated in this work as the "density functional approximation" (DFA) not to be confused with density functional theory (DFT) (see below). Indeed, the notation "Wigner-type density functional", used by Clementi in the past 40 years seems to have not conveyed the idea of the difference between DFA and DFT.

Soon thereafter, Hohenberg and Kohn, also in California, published a theorem [37] proposing a unique relation between exact electronic density and exact wavefunctions for non-degenerate states (thus a theorem for semi-classical systems), without, however, providing any algorithm to link density and energy.

We recall that the Thomas–Fermi [38,39] approximation for atomic systems, based on the Poisson equation, is also density related; however, this approximation was disregarded in the early development of quantum chemistry, due to the opinion that it could not lead to any molecular binding. In the late 1950s there was a renew interest [40] and today we know that about 50% of the molecular binding can be obtained with classical considerations without inclusion of the exchange term [41].

The idea to introduce correlation via modifications of the HF interactions, e.g., with the Coulomb hole [30] or with Wigner-type density functionals [25–29], is also central in the Slater‘s proposal to extend the role of the HF exchange energy, leading eventually to the "xα" approximation [42]. Recall that Slater had already suggested how to simplify the computation of the exchange energy [43] particularly cumbersome in solid state computations; this suggestion did lead to Hermann and Skillman tables of atomic functions [44]. Thus DFA are recurring concepts from mid-1930 to mid-1960.

The Thomas–Fermi model was assumed as a starting point in the paper by Kohn and Sham [45] which, however, presented two very distinct avenues. The first one is a typical DFA approach, which restates the concepts provided by the Coulomb hole [30] computations and by the "xα" approximation [42,44]; the resulting orbitals are the so-called Kohn–Sham orbitals, and the approximation did eventually lead —after a number of years– to a most popular type of molecular computations, the so-called Kohn–Sham DFT molecular approximation, popularized for example by Parr and Yang volume [46] but mostly by the availability of easy to use computer codes [47,48]. We are of the opinion that "Kohn–Sham DFA" and not Kohn–Sham DFT is the correct label for this approach. The second avenue [45] proposes the Hohenberg and Kohn theorem as the base for a new way to obtain exact energies, from exact densities, conditioned, however, to the availability of an exact exchange expression; till now there is no such expression. Indeed, the electronic density, being spin independent, is a questionable starting point for defining a spin dependent exchange energy. This second avenue is designated DFT.

We stress the difference of the DFT from the DFA proposals: in the DFA approach explicit semi-empirical corrections are inserted into the traditional HF computations, maintained as the theoretical foundation; in the DFT approach, the HF approximation is explicitly eliminated in favor of a new method requiring, however, a "new exchange" formulation, based on the spin-independent electronic density. Particularly critical for the DFT avenue is the computation of excited states, since these require vector coupling coefficients, which, however, assume the HF wave-function framework. The two view points are not compatible, due to the opposing starting assumptions.

Parallel to these developments based on the variational method, the introduction of perturbation methods in 1934 with Møller and Plesset [49] opened new avenues, leading eventually to the coupled cluster methods [50,51] 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 [52].

However, it does not seem incorrect to state that none of the above methods is adequate to provide an ab initio computationally efficient solution of the Schrödinger equation. Indeed, it does not surprise that in the meantime "magic formulae" had become very popular among pragmatic chemists, a consequence of the realization that quantum chemical computations can provide predictions and explanations in many facets of chemistry not only for small molecules (two to ten atoms, the ab initio chemistry area) but also for larger molecular systems with up to hundred(s) of atoms. Availability of *easy to use* computer codes [47,48], and the computerization of sciences are two additional determining factors for the diffusion of semi-empirical methods. For details we refer to relatively recent publications [19,20] presenting different view points on the present status [19] and the evolution [20] of quantum chemistry, respectively.

Presently, there is still some debate on the ab initio versus semi-empirical nature of some of the above algorithms. Actually, the answer is trivial to researchers able to read a computer code: indeed, if semi-empirical parameters or approximations are used to compute the energy of the system in examination, then the method and the algorithm is semi-empirical. (Note, however, that often the users of quantum chemical computer codes do not to care about the underlining method of the selected code, being interested mainly in the computed results).

We recall a few among of the many semi-empirical avenues; we start by mentioning the extension of Hückel-type Hamiltonians [53] and the many applications of the molecular mechanics approximation [54]; other methods, like differential overlap techniques [55], appear today to be more and more obsolete.

Among the post-HF semi-empirical models we recall modifications of Clementi's Coulomb hole [30] leading to new formulations for atomic [56,57] and molecular orbitals [58,59] in the HF frame, or to extensions for more than a single HF configuration [60,61], or for spinors [62].

Another semi-empirical post-HF application, even if today somewhat in decline, is the "xα" approximation [42]. Finally, in this partial list of semi-empirical approximations, we must add, as previously stated, the today very popular Kohn–Sham DFA semi-empirical approximations [45–48] often (unfortunately) presented as ab initio computation.

1.2 A justification

We hasten to call to mind that today there are different and appealing alternatives [19] to the approaches mentioned above and the methodological effort continues for the applicability of quantum chemical methods to very large and complex systems with increasingly reliable methods. Molecular dynamics (MD) is by now more and more a chapter of quantum chemistry; it provides the possibility to deal with very large chemical systems, and presents the enormous advantage to deal explicitly with time, temperature and thermodynamics, the heart of chemistry.

From a historical point of view, the pragmatic rush to develop new techniques and methods has understandably left numerous gaps. In addition, in the early days the enthusiasm and a highly competitive atmosphere in the new field of computational chemistry highlighted the differences rather than the complementary nature of the two traditional and competing quantum chemical approaches, HF and VB. Today, we can afford a more relaxed attitude, and continue on Herzberg's trail [6], where the study of the ground state binding energy and of molecular spectra is explained with reference to both the MO and the HL methods.

We stress that Herzberg classical analysis, being prior to the advent of computer programs in computational chemistry, is nevertheless capable of providing very instructive explanations on binding energy, both for ground and excited states, based on relatively few electronic configurations or on a few electron pairs. This old, albeit qualitative approach appears to be in contrast to today somewhat diffuse mentality in computational chemistry, indifferent to its inability to provide physical and chemical explanations and bent on promoting computer intensive methods, unfortunately often valid only for small molecular systems. Recall that full CI and MC–SCF were referred in the early 1960s as "brute force methods", because of their nearly total reliance on the ever increasing power of computational devices.

Even at the risk of overextend this already lengthy section, we cannot refrain from reporting a few lines from C. A. Coulson's closing address [63] at a quantum chemistry milestone, the 1960 Boulder Colorado meeting, concerning what laboratory chemists likely want from quantum chemists, for example in answering why the H–F bond is so strong, when the F–F bond is so weak "... any explanation "why" must be given in terms of concepts which are regarded adequate and suitable. So the explanation must not be that the electronic computer shows that D (H–F) $\gg$ D (F–F), since this is not an explanation at all, but merely a confirmation of experiment. Any acceptable explanation must be in terms of repulsion between non-bonding electrons, dispersion force, between the atomic core, hybridization, and ionic character. It does not matter that in the last resort none of thee concepts can be made rigorous".

1.3 Back to the main task

In a few situations, the two 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 equal accuracy at any internuclear separation.

Parenthetically we note, following Hirschfelder [64], that "molecular forces" can not be "explained with" but only "correlated to" partitioning of the electronic density; any explanation of "molecular forces" requires specific theoretical and computational approaches dealing with analyses of forces; for example, those proposed long ago by Hellmann [65] and Feynman [66] and implemented for example in the recent work by Fernandez Rico et al. [67].

This paper makes use of a recent preliminary proposal [68] on the Hartree–Fock–Heitler–London (HF–HL) method and of computations on diatomic hydride [69,70] and homopolar [71] molecules.

2 The HF–HL first step

The HF–HL algorithm is formally proposed as a three-step process with increasing accuracy at each successive step; alternatively, the HF–HL method can be considered as a model with two physical approximation levels, where we account for non-dynamical correlation (computationally, it corresponds to the "first HF–HL" step) and the post-HF–HL model, where we account also for the dynamical correlation (computationally, this is the "second" and "third HF–HL step").

2.1 The first HF–HL step

In the first step, we variationally combine the HF and the HL functions, the latter being built with HF atoms [68,69] thus yielding by construction correct dissociation products. The HF and HL functions are improved, via short MC expansions, to introduce near-degeneracy correlation energy (see Sect. 3) and avoided state crossing, whenever the state in consideration results from an avoided potential energy curve crossing. In this way, the HF–HL function accounts for the non-dynamical correlation energy. The HF and the HL functions can be further improved by considering additional expansion terms, either MC–HF or MC–HL (for example, the so-called "ionic structures"), but, since these extensions bring about dynamical correlation, we defer its consideration to post HF–HL computations (see Sect. 5).

Formally, we start by defining with obvious notation Ψ_{HF}, and the Ψ_{HL} functions given in Eqs. 1a and 2a, respectively:

$$\Psi_{\mathrm{HF}} = \det(\Phi_1, \ldots, \Phi_\mathrm{i}, \ldots, \Phi_\mathrm{n}) \tag{1a}$$

$$\Psi_{\mathrm{HL}} = \Sigma_\mathrm{k} \det(\varphi_{1\mathrm{k}}, .., \varphi_{\mathrm{ik}}, \ldots, \varphi_{\mathrm{mk}}) \tag{2a}$$

Above, Φ_i refers to ith HF molecular orbital and φ_{lk} to the lth atomic orbital of the kth determinant in the HL function. Note that the HL functions are constructed to satisfy the correct spin coupling constrains [72].

When at dissociation the atoms in the molecule are in a state with near-degeneracy (e.g., 2s–2p for second row atoms) and/or when there is avoided crossing, then in Eqs. 1a and 2a the Ψ_{HF} and the Ψ_{HL} are replaced with very short MC expansions, designated Ψ_{HF} and Ψ_{HL} accounting for near-degeneracy and avoided crossing, leading to

$$\Psi_{\mathrm{HF}} = \Sigma_\mathrm{t} a_\mathrm{t} \Psi_{\mathrm{HF(t)}} = \Sigma_\mathrm{t} a_\mathrm{t} [\det(\Phi_1, \ldots, \Phi_\mathrm{i}, \ldots, \Phi_\mathrm{n})_\mathrm{t}] \tag{1b}$$

$$\Psi_{\mathrm{HL}} = \Sigma_\mathrm{t} b_\mathrm{t} \Psi_{\mathrm{HL(t)}} = \Sigma_\mathrm{t} b_\mathrm{t} \Sigma_\mathrm{k} [\det(\varphi_{1\mathrm{k}}, .., \varphi_{\mathrm{ik}}, \ldots, \varphi_{\mathrm{mk}})]_\mathrm{t} \tag{2b}$$

where the a_t and b_t are the weights of the MC expansions.

The HF–HL wavefunction $\Psi_{\mathrm{HF-HL}}$ is obtained by determining variationally the linear combination

$$\Psi_{\mathrm{HF-HL}} = \Sigma_\mathrm{t} a_\mathrm{t} \Psi_{\mathrm{HF(t)}} + \Sigma_\mathrm{t} b_\mathrm{t} \Psi_{\mathrm{HL(t)}} \tag{3}$$

In Sect. 3 we shall introduce a specific notation to characterize the length and the specific terms in the expansions for Ψ_{HF} and for Ψ_{HL}.

In Eq. 3 the a_t and b_t coefficients are obtained variationally by solving the equation

$$(\mathbf{H} - \mathbf{SE})\mathbf{C} = \mathbf{0} \tag{4}$$

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 of Gaussian functions and the same basis set is also used to expand the orbital φ_{lk} of Ψ_{HL}. We recall that the Φ_i orbitals form an orthogonal set, whereas the φ_{lk} orbitals can be non-orthogonal. For the latter case, following Löwdin [73] the interaction between two determinants, d_a and d_b, is given by:

$$\langle \mathrm{d}_a|\mathrm{H}|\mathrm{d}_b\rangle = \sum\nolimits_{\mathrm{ij}} \mathrm{h}_{\mathrm{ij}} \mathrm{S}^{(\mathrm{i,j})} + \sum\nolimits_{\mathrm{i<k,j<l}} [\langle \mathrm{ij}|\mathrm{kl}\rangle - \langle \mathrm{il}|\mathrm{kj}\rangle] \mathrm{S}^{(\mathrm{i,k,j,l})} \tag{5}$$

where the indices i and k refer to the occupied orbitals of d_a and j and l to those of d_b; $\mathrm{S}^{(\mathrm{i,j})}$ and $\mathrm{S}^{(\mathrm{i,k,j,l})}$ are the first- and second-order cofactors of the overlap matrix **S**, constructed with the occupied orbitals of d_a and d_b. The cofactors are computed with the algorithm proposed in [74] adapting routines from the public domain Linpack library [75]. The formulation of second and the third HF–HL steps, namely, the post-HF–HL method is explained in Sect. 5.

3 Dynamical and non-dynamical correlation energy and the HF–HL model

3.1 Decomposition of correlation effects

The standard definition of the correlation energy [76] relates specifically to the HF method. Therefore, since we consider also the HL and the HF–HL methods we need a more general definition and an appropriate notation for the correlation energy associated with the HF–HL model.

Molecules are systems of nuclei and electrons, and the correlation energy can be defined with reference to an expansion into one-, two-,..., many-electron energies obtained by solving the corresponding one-, two-,..., many-electron exact solutions. The existing approximated solution from a given non-relativistic model (like HF, HL, HF–HL) brings about energy differences relative to the energies obtained (a) with the exact one-electron non-relativistic model, difference called "non-dynamical" correlation, E_c (non-dyn), and (b) with the exact many-electron non-relativistic model, the total correlation energy, E_c. The difference between the total and the non-dynamical correlation energy is, by definition, the dynamical correlation energy, E_c(dyn). This view point follows most naturally the HF approach.

Alternatively, particularly considering the HL approach, we can 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, $\Sigma_a\epsilon_a$, is the sum of the correlation corrections for each individual atom, ϵ_a, and the second, $\eta_M = (E_c - \Sigma_a\epsilon_a)$, is the "molecular extra-correlation energy" [77]. This second viewpoint is complementary to the previous one, and

$$\mathrm{E_c} = \Sigma_a\epsilon_a + \eta_M \tag{6}$$

is the starting point for the decomposition given in Sect. 3.3.

3.2 Non-dynamical correlation energy

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. Essentially, the non-dynamical correlation corrects for gross deficiencies of the HF one electron model and cannot be considered a true many-body effect. Let us consider near-degeneracy. The non-dynamical correlation has been accounted by Hartree et al. [12] 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 based on perturbation methods was proposed by Sinanoglu [78,79]. Following Hartree et al. [12], Veillard and Clementi [80] computed with Slater-type functions E_c(non-dyn) for the second-row atoms and ions using an MC expansion of two configurations, the ground state configuration $1s^22s^22p^n$ and its degenerate $1s^22s^02p^{n+2}$. These computations have been reproduced [69] with extended Gaussian basis, including recently the iso-electronic series of positive ions till $Z = 10$ [81] ; for Be [^{1}S], B[^{2}P] and C[^{3}P] atoms the non-dynamical correlation energies are 0.04372, 0.03481, and 0.01936 hartree, respectively, in substantial agreement with the computation by Veillard and Clementi [80], showing that relatively small amount of mixing is sufficient to remove near-degeneracy errors in atoms.

Concerning the constraint of doubly orbital occupancy, we recall that the HF model approaching dissociation can become unstable leading to grossly incorrect energies. The use of the unrestricted HF algorithm avoids this catastrophic behavior, but the resulting wavefunction is incorrect. An alternative, proposed by Lie et al. [60,61] was to determine a short MC function, ensuring proper dissociation, gaining in addition most of the non-dynamical correlation energy. This approach was the first computation in quantum chemistry using density functionals—in the DFA spirit—to correct MC rather than HF functions. The approach is not of easy implementation for molecules with more than two atoms and for multiple bonds. For example, even in the ground state of N_2 ten configurations are needed to obtain correct dissociation [60,61], to be compared with only two configurations (one from HF and one from HL) in the HF–HL model.

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 [6,69] as in, for example, BeH. 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.

3.3 Model-dependent partitioning of correlation energy

We have partitioned the total molecular correlation energy E_c into the sum of $\Sigma_a\epsilon_a$ and η_M; recalling the partitioning into dynamical and non-dynamical component

$$\begin{aligned}E_c = &\sum_a[\epsilon_a(\text{dyn}) + \Sigma_a\epsilon_a(\text{non-dyn})]\\ &+\eta_M(\text{dyn}) + \eta_M(\text{non-dyn})\end{aligned} \tag{7}$$

Since the correlation errors are model dependent, we must distinguish $\mathrm{E_{c(HF)}}$ from $\mathrm{E_{c(HL)}}$, and write:

$$\begin{aligned}E_{c(HF)} = &\Sigma_a\epsilon_{a(HF)}(\text{non-dyn}) + \Sigma_a\epsilon_{a(HF)}(\text{dyn})\\ &+\eta_{M(HF)}(\text{non-dyn}) + \eta_{M(HF)}(\text{dyn})\end{aligned} \tag{8a}$$

$$\begin{aligned}E_{c(HL)} = &\Sigma_a\epsilon_{a(HL)}(\text{non-dyn}) + \Sigma_a\epsilon_{a(HL)}(\text{dyn})\\ &+\eta_{M(HL)}(\text{non-dyn}) + \eta_{M(HL)}(\text{dyn})\end{aligned} \tag{8b}$$

In the HF–HL method, $\Sigma_a \epsilon_a$(non-dyn) is accounted by the inclusion of near-degeneracy and avoided crossing, and η_M(non-dyn) by ensuring correct dissociation with the HL function: thus for the HF–HL model the correlation correction is reduced to

$$E_{C(HF-HL)} = \eta_{M(HF-HL)}(\text{dyn}) + \Sigma_a \epsilon_{a(HF-HL)}(\text{dyn}) \tag{9}$$

The terms in Eq. 9 can be decomposed with the traditional [32,33] sub-partitioning into intra-pair, e_{ii}, and inter-pair, e_{ij}, electron correlation. Due to chemistry interest in the binding energy, we are particularly interested in intra- and inter-pair electron correlation related to binding orbitals and specific atoms in the molecule. In the Appendix we expand on this point.

3.4 Notation

Previously [69], we have introduced definitions and a specific notation needed to ensure a coherent discussion in the HF–HL method. We indicate as MC–HF and MC–HL multi-configuration expansions of HF-type and HL-type functions, respectively. When needed, we use the specific notation HF(n), HL(m) and HF–HL(n, m) to designate MC–HF expansions of n configurations, MC–HL expansions of m configurations, and HF–HL function composed by the linear combination of HF(n) and HL(m). The energies $E_{HF}(n)$, $E_{HL}(m)$ and $E_{HF-HL}(n, m)$ correspond to the wave functions HF(n), HL(m) and HF-HL(n, m), respectively. Equivalent notation is used for the computed binding energies, E_b, and the correlation energies, E_c. To indicate a specific electronic configuration within a given MC expansion we use the notation HF-n, HL-m.

4 Diatomic molecules and HF–HL first step computations

The HF–HL method—in its simplest implementation (first step)— accounts for the non-dynamical correlation energy and explicitly considers avoided crossing. With the simple HF–HL model we have computed [68,69] the ground state potential energy curves for the first and second row hydrides, obtaining in average 80% of the experimental binding energy, to be compared with 60 and 70% from HL and HF computation, 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 we obtain 66% of the experimental binding, compared with 48% and 32 from HF and HL computations. (F_2 is repulsive in the HF model and the same holds for B_2 and F_2 in the HL model).

Below, we briefly comment on the HF–HL first step computations on hydrade and homopolar molecules, selecting the $H_2[^1\Sigma_g^+]$, LiH$[^1\Sigma^+]$, HF$[^1\Sigma^+]$, $Li_2[^1\Sigma_g^+]$, $N_2[^1\Sigma_g^+]$, and $F_2[^1\Sigma_g^+]$ ground states as examples for a more detailed analysis, since either composed with the first or last atom of an atomic period, $H_2[^1\Sigma_g^+]$, LiH$[^1\Sigma^+]$, HF$[^1\Sigma^+]$, $Li_2[^1\Sigma_g^+]$, and $F_2[^1\Sigma_g^+]$, or with a multiple bond, $N_2[^1\Sigma_g^+]$. For additional data on the original computations, see [68–72].

In Table 1 we report for the hydride ground states the experimental binding energy, the corresponding equilibrium internuclear separation, exact non-relativistic energies at

Table 1 Diatomic hydrides: laboratory molecular binding energy (kcal/mol), E_b, laboratory equilibrium distance(bohr), R_e, total exact non-relativistic energy at equilibrium, $E_T(R_e)$, and at dissociation, $E_T(R_\infty)$, atomic HF energies (hartree), E_{HF}(limit), and E_{HF} (this work)

Molecule	$E_b^{[a]}$	$R_e^{[a]}$	$E_T[R_e]$	$E_T[R_\infty]$	E_{HF} [limit]		E_{HF} [this work]
$H_2[^1\Sigma_g^+]$	109.48[b]	1.4[b]	−1.1744757	−1.000000	H $[^2S]$	−0.500000	−0.499999
HeH $[^2\Sigma^+]$	0.01[c]	7.00	−3.4037459	−3.4037243	He $[^1S]$	−2.861680	−2.861679
LiH $[^1\Sigma^+]$	58.00	3.0150	−8.070491	−7.978062	Li $[^2S]$	−7.432727	−7.432721
BeH $[^2\Sigma^+]$	49.83[d]	2.5371	−15.246772	−15.167363	Be $[^1S]$	−14.573023	−14.573016
BH $[^1\Sigma^+]$	84.1[e]	2.3289	−25.28795	−25.15393	B $[^2P]$	−24.529061	−24.529036
CH $[^2\Pi]$	83.9	2.1163	−38.47869	−38.34499	C $[^3P]$	−37.688619	−37.688616
NH $[^3\Sigma^-]$	80.5[f]	1.9582	−55.21754	−55.08925	N$[^4S]$	−54.400934	−54.400924
OH $[^2\Pi]$	106.6	1.8324	−75.73708	−75.5672	O $[^3P]$	−74.809398	−74.809384
HF $[^1\Sigma^+]$	141.5[g]	1.7325	−100.4592	−100.2337	F$[^2P]$	−99.409349	−99.409343

[a] Ref. [82]
[b] Ref. [83]
[c] Ref. [84]
[d] Ref. [85]
[e] Ref. [86]
[f] Ref. [87]
[g] Ref. [88]

equilibrium and at dissociation, atomic energies at the HF limit and computed [68,69] with Gaussian basis sets. The basis sets we have used are extended basis sets of the Gaussian functions with several polarization functions such as to ensure not only HF limit atomic energies but also correlation corrections. Table 2 reports equivalent data for the homopolar molecules.

In Fig. 1 we report, for the above molecules, the ground state potential energy curves computed with the HF, HL and HF–HL approximations. The number of computations at different internuclear separations varies from 20 to 30. In general, the HF–HL improvement over the traditional methods is larger in the homopolar molecules than in the hydrides.

In Fig. 2 we display the gain in the computed ab initio binding energy for the full set of hydrides (top inset) and homopolar (bottom inset) relative to HF computations: we

Table 2 Laboratory molecular binding energy (kcal/mol), E_b, laboratory equilibrium distance (bohr), R_e, non-relativistic energy at equilibrium, $E_T(R_e)$, and at dissociation, $E_T(R_\infty)$

Molecule	$E_b^{[a]}$	$R_e^{[a]}$	$E_T[R_e]$	$E_T[R_\infty]$
$H_2[^1\Sigma_g^+]$	109.48[b]	1.4[b]	−1.1744757	−1.000000
$Li_2[^1\Sigma_g^+]$	24.67	5.051	−14.99543	−14.95612
$Be_2[^1\Sigma_g^+]$	2.40[c]	4.63	−29.33860	−29.33478
$B_2[^3\Sigma_g^-]$	71.14	3.0047	−49.42117	−49.30780
$C_2[^1\Sigma_g^+]$	145.86	2.348	−75.9224	−75.6900
$N_2[^1\Sigma_g^+]$	228.4	2.0743	−109.5426	−150.1348
$O_2[^3\Sigma_g^-]$	120.6	2.2819	−150.3270	−199.4682
$F_2[^1\Sigma_g^+]$	39.0	2.6682	−199.5304	−257.8766

[a] Ref. [82]
[b] Ref. [83]
[c] Ref. [89]

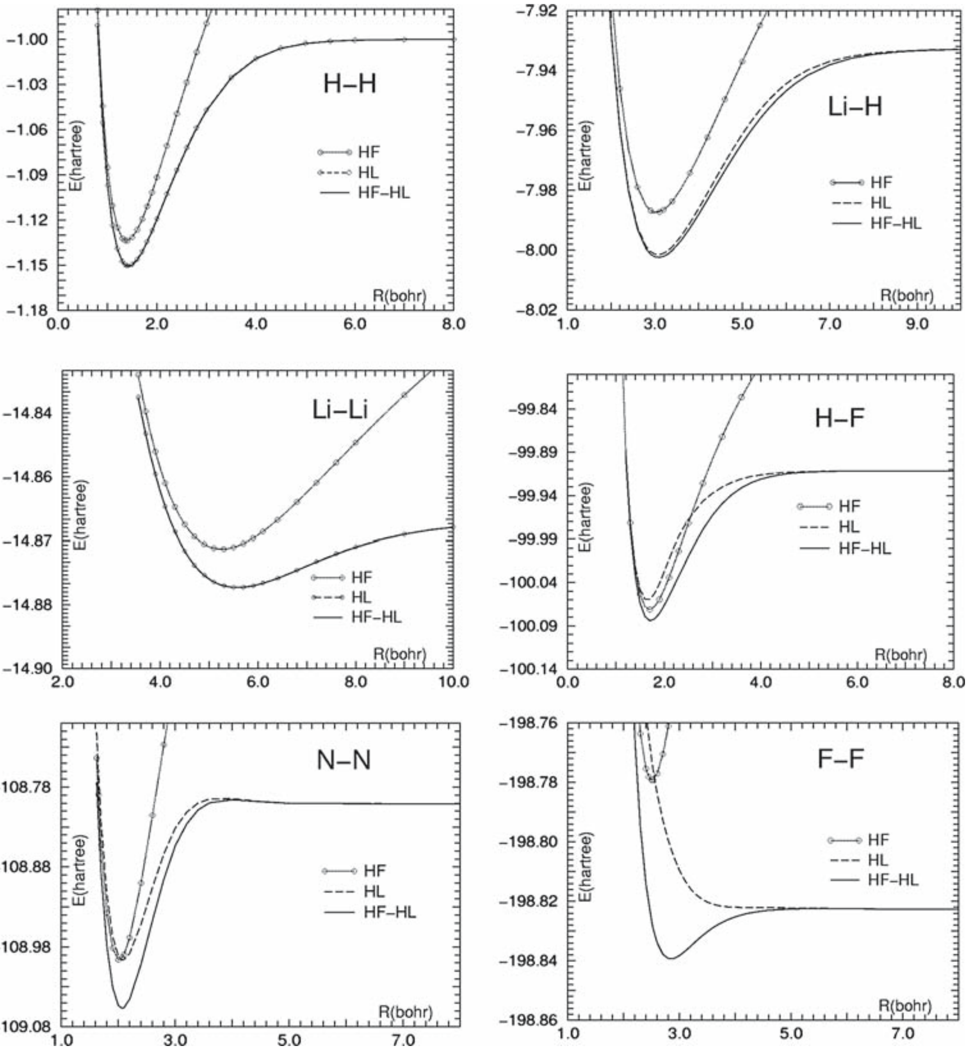

Fig. 1 Potential energy curves from first step HF, HL, and HF–HL computations for $H_2[^1\Sigma_g^+]$, $LiH[^1\Sigma^+]$, $HF[^1\Sigma^+]$, $Li_2[^1\Sigma_g^+]$, $N_2[^1\Sigma_g^+]$, and $F_2[^1\Sigma_g^+]$

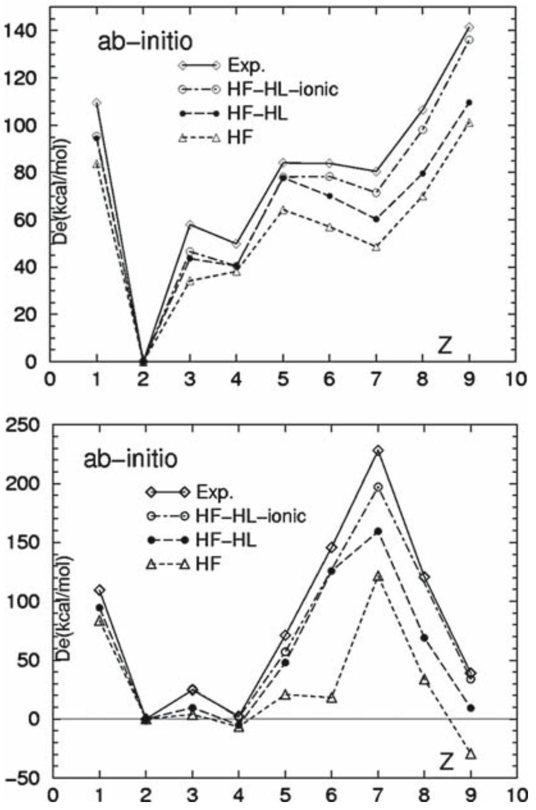

Fig. 2 *Top* hydride binding energies from ab initio HF and HF–HL approximations, with and without ionic configurations, and experimental binding. *Bottom* same for homopolar diatomic molecules

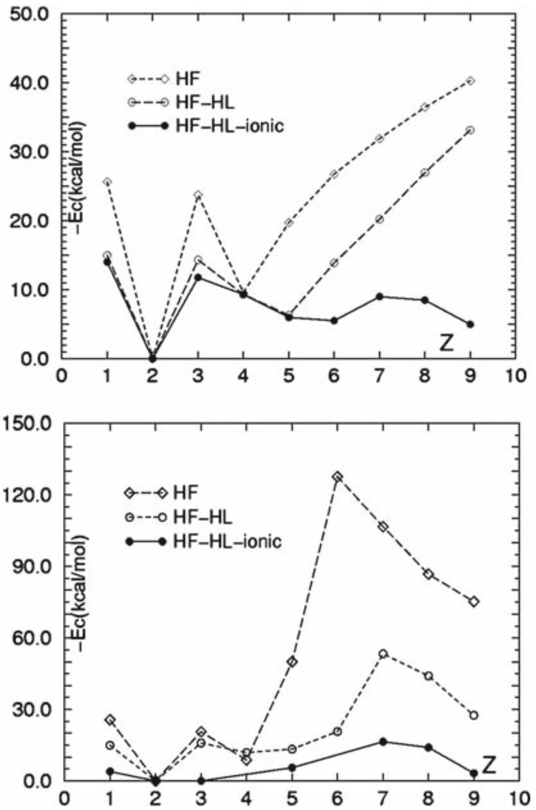

Fig. 3 *Top* hydride molecular extra correlation energies from the HF and HF–HL approximations. *Bottom* same for homopolar diatomic molecules

report binding energy from HF, HF–HL without and with inclusion of ionic structures. The gains due to inclusion of the ionic structures are notable, bringing the agreement with the experimental binding from 80 to 91%. These computations will be discussed below in Sect. 5.2, since the resulting energies belong to post-HF–HL computations.

In Fig. 2 we have not reported equivalent comparison with the HL method, since the binding energies are in average inferior to those of the HF method. For the homopolar molecules, the ionic structures thus far preliminarily considered are limited to Li_2, B_2, N_2, O_2, and F_2. Computations on the ground state of Be_2 and on the ground and excited states of C_2 are given in Ref. [71].

With Fig. 3 we complement Fig. 2 by reporting the error in the binding energy, namely the molecular extra correlation energy; the top insert relates to the hydrides, the bottom to the homopolar molecules. These residual errors are due to the neglect of a few intra-pair correlation contributions e_{ij} discussed in Eq. 8A of the appendix (recall that $e_{ii} \gg e_{ij}$ and $e_{jj} \gg e_{ij}$).

The binding energy gains, relative to the HF and the HL models, are most evident and need no comment. The HF–HL, indeed, emerges as the general zero-order approximation for quantum chemistry, namely, the "reference function", which qualitatively approximates laboratory data consistently and with equal accuracy at any internuclear separation with a simple wavefunction. The computations with ionic structures for homopolar molecules are in progress to complete the study, but it is clear that the ab initio HF–HL model yields with very few configurations nearly correct binding energies.

5 Ab initio post-HF–HL

The dynamical correlation is accounted in the post-HF–HL method, either ab initio or semi-empirically, depending on the molecular complexity and available computational facilities. We are of the opinion that to lump the many and different correlation energy effects into a single "error" is probably an unfortunate misconception, widely accepted in past and present quantum chemistry, and perhaps partly responsible for the slow progress. Indeed, the use of different algorithms to correct specific correlation effects allows a multiplicity of correction strategies, each one specific for a given correlation subtask.

Above, we have tackled the non-dynamical correlation correction with success; below we shall deal with the dynamical correlation problem in two ways, either following the traditional approach, namely with the use of a single algorithm, or exploring the feasibility of corrections with a step by step approach.

Within the traditional approach one corrects a given model (HF, HL or HF–HL) either with ab initio techniques or, alternatively, with semi-empirical methods, for example with the density functional approximations. In this section, we discuss two ab initio post-HF–HL algorithms. In the first (see Sect. 5.1) we rely on MC–HF and MC–HL expansions and therefore we are limited to relatively few electrons. The second includes ionic structures and yields notable improvements to the binding energy, as mentioned in the discussion of Figs. 2 and 3 (see Sect. 5.2).

5.1 Ab initio post-HF–HL computations

Keeping in mind the decomposition of dynamical correlation energy into two components, i.e. a molecular component (the molecular extra correlation) and an atomic component (the sum of dynamical correlation energy of the separated atoms), we propose two steps, designated second and third HF–HL steps, respectively. The correlation techniques adopted in the second and third steps are adaptations of MC expansions.

In the post-HF–HL method, the dynamical correlation correction is obtained by replacing in Eq. 1 the Ψ_{HF} function with an extended MC–HF linear expansion of HF-type functions, $\Sigma_p a_p \Psi_{p(\mathrm{HF})}$ and the Ψ_{HL} with an MC–HL expansion of HL-type functions, $\Sigma_q \mathrm{b}_q \Psi_{\mathrm{q(HL)}}$:

$$\Psi'_{\mathrm{HF-HL}} = \Sigma_p a_p \Psi_{p(\mathrm{HF})} + \Sigma_q b_q \Psi_{\mathrm{q(HL)}} \tag{10}$$

the p, q, indices define excited configurations of the MC expansions and a_p, b_q, are the corresponding variational expansion coefficients. The two MC expansions complement one another and Eq. 10 constitutes the *second HF–HL step*. In this step, ionic structures in $\Sigma_q b_q \Psi_{q(\mathrm{HL})}$ are particularly efficient since provide for in-out correlation (see Sect. 5.2). Note that in a previous study [68] we have leaned that the convergence rate for MC–HF expansion is very similar to the convergence rate in MC–HL expansions.

The remaining dynamical correlation energy, related to inner shell and non-bonding electrons, is computed by solving Eq. 11, the *third step* of the ab initio post-HF–HL approach:

$$\Psi_{\mathrm{HF-HL}} = \Sigma_P a_P \Psi_{P(\mathrm{HF})} + [\Sigma_q b_q \Psi_{q(\mathrm{HL})} + \Sigma_r b'_r \Psi_{r(\mathrm{HL})}] \tag{11}$$

In Eq. 11 the index P replaces p of Eq. 10 to indicate a more extended expansion. For the HL component we propose two MC–HL linear expansions, one $\Sigma_q b_q \Psi_q$ (present also in Eq. 10) with optimized atomic orbitals, the second $\Sigma_r b'_r \Psi_r$ (generally an extended expansion) constructed by adapting to the HL model MC–HF functions originally computed, once for always, for the separated atoms. The latter is intended to be used over and over for different molecules in HF–HL computations containing atoms with the same Z number and state specification, thus transferable from molecule to molecule, as very preliminarily exemplified by the HF–HL computations on the LiH and $\mathrm{Li_2}$ molecules [68]. For polyatomic systems the transferability of $\Sigma_r b'_r \Psi_{r(\mathrm{HL})}$ is expected to become an important feature the larger the system in consideration.

For a few electron systems, the dynamical correlation can be obtained simply via very extensive CASSCF computations, namely, neglecting the MC–HL expansion and considering only expansions of CASSCF type. Computations of this type have been restricted to simple systems, namely, $\mathrm{H_2}$, HeH, LiH, and BeH yielding at equilibrium the following accurate binding energies (in kcal/mol): for $\mathrm{H_2}[^1\Sigma_g^+]$ 109.26, for HeH $[^2\Sigma^+]$ 0.021, for LiH$[^1\Sigma^+]$ 57.68 and for BeH $[^2\Sigma^+]$ 49.61. Computations for the binding energy using Eq. 11 with both the MC–HF and MC–HL expansions yield for $\mathrm{H_2}[^1\Sigma_g^+]$, LiH$[^1\Sigma^+]$, and $\mathrm{Li_2}[^1\Sigma_g^+]$ ground state the following reasonable binding energies [68] (in kcal/mol) 108.56, 57.32 and 23.83, respectively, requiring only 6, 98 and 94 configurations, respectively.

5.2 Computation of $\eta_{\mathrm{M(HF-HL)}}(\mathrm{dyn})$

Note that, generally, in ab initio computations, the aim is to compute the total correlation error, but if this task is too complex, we might be contented to account for part of the dynamical correlation, particularly the molecular extra correlation, $\eta_{\mathrm{M(HF-HL)}}(\mathrm{dyn})$, thus allowing accurate binding energy predictions.

It is known [69,90] that inclusion of ionic structures in the HF–HL functions improves the computed binding energy; below we consider this avenue in detail. Note that in Eq. 3 we have not included ionic structures in the HL component, since this would have accounted for a fraction of the total dynamical correlation, a task left to post-HF–HL computations. Incidentally, unknown to most of the quantum chemical literature, the use of ionic structures in quantum chemical computations dated back to a paper by Majorana [91] in 1931, where the celebrated Heitler London computation [7] was improved by adding $\mathrm{H^+H^-}$ pairs with a $2\mathrm{p}_\sigma$ orbital in the $\mathrm{H^-}$ configuration. The ionic structures $\mathrm{H^-X^+}$ and $\mathrm{H^+X^-}$ for the HX hydrides considered in this work are designated “basic ionic” structures, and at dissociation yield $\mathrm{H^-}$ in the $^1\mathrm{S}(1\mathrm{s}^2)$ state and $\mathrm{X^+}$ and $\mathrm{X^-}$ ions constrained to be in a state of the lowest configuration, fulfilling Wigner–Witmer [92] and Mulliken [93] dissociation rules, reported also in the classical volume by Hertzberg [6].

Table 3 Ionic HF–HL binding energy, E_b(HF–HL)$_i$ (kcal/mol), total energy (hartree) at equilibrium, E(HF–HL)$_i$(R_e), and at dissociation, E(HF–HL)$_i$(R_∞). Work in progress

Molecule	E_b(HF–HL)$_i$	$-E$(HF–HL)$_i$(Re)	$-E$(HF–HL)$_i$(R_∞)
$H_2[^1\Sigma_g^+]$	95.42	1.15207	1.00000
LiH $[^1\Sigma^+]$	46.59	8.00699	7.93274
BeH $[^2\Sigma^+]$	45.73	15.18961	15.11673
BH $[^1\Sigma^+]$	78.10	25.18831	25.06384
CH $[^2\Pi]$	78.39	38.33102	38.20610
NH $[^3\Sigma^-]$	71.50	55.01548	54.90153
OH $[^2\Pi]$	98.11	75.46883	75.31028
HF $[^1\Sigma^+]$	136.12	100.12830	99.91138
$Li_2[^1\Sigma_g^+]$	25.48	14.90646	14.86544
$B_2[^3\Sigma_g^-]$	62.95	49.22392	49.12360
$N_2[^1\Sigma_g^+]$	213.10	109.13953	108.80184
$O_2[^3\Sigma_g^-]$	110.25	149.78905	149.61924
$F_2[^1\Sigma_g^+]$	35.70	198.87700	198.81916

Using the basis sets given in [69] for the hydrides we have computed HF–HL functions with inclusion of the “basic ionic” structures. The gain in the binding energy relatively to HF–HL covalent computations is appreciable, as shown in Figs. 2 and 3. In Table 3 we report for the hydride the computed binding energy, E_b(HF–HL)$_i$ (in kcal/mol), the computed total energy at equilibrium, E(HF–HL)$_i$(Re), and at dissociation, E(HF–HL)$_i$(R_∞) (in hartree). At the bottom of Table 3 we have added the data for Li_2, B_2, N_2, O_2, and F_2. Some of the data reported in the table, particularly for B_2, N_2, O_2, are only partially optimized; work is in progress.

Let us now briefly consider the H_2 molecule for which we have added to the covalent HF–HL configuration a Majorana type structure $H^-(2p_\sigma^2, {}^1S) - H^+$. The corresponding binding energy is 100.24 kcal/mol compared with 95.42, by considering the basic ionic structures, and 94.50 from only the covalent configuration.

The ionic structures in the homopolar molecules yield binding energies close to the experimental values. Note, however, that the ionic structures can contribute also to the inner shell energy, as indicated by the Li_2 binding. The computed Li_2 binding energy is somewhat larger than the experimental value; the ionic structures can improve the energy more near equilibrium than at dissociation.

The inclusion of ionic structures reported in this work is likely a preliminary step for a more general analysis on the in–out correlation, related to the atomic radial correlation long ago considered for the first and second row atoms by Clementi et al. [94]. We would be not surprised if an extensive analysis will bring about 100% of the binding energy still with relatively few ab initio HF–HL configurations.

6 Post-HF–HL via density functional approximation, DFA

Recall that in the post-HF–HL method the dynamical correlation can be introduced with a variety of alternative techniques either ab initio or semi-empirically [95]. The extensive computations by Lie et al. for diatomic homopolar molecules [61] and hydrides [60] have clearly shown that density functional approximations applied to MC expansions (computed to correct the HF function near dissociation), yield reasonable binding and total energies. Note that for HF–HL functions the correct dissociation is ensured by construction, thus available and tested semi-empirical density functionals [25–30,56–61] obtained within the DFA spirit can be used to deal with the dynamical correlation. In the following, we use the Coulomb hole, Ch, DFA approach [58,59].

The Coulomb hole corrects the HF Coulomb interaction, which is overestimated in the HF approximation because of the use of the same orbital for a pair of electrons. There are different algorithms for the Coulomb hole. The specific algorithm for this work is the soft Coulomb hole Ch functional re-calibrated for molecular computations [58,81] making use of new reliable correlation energy estimates [96].

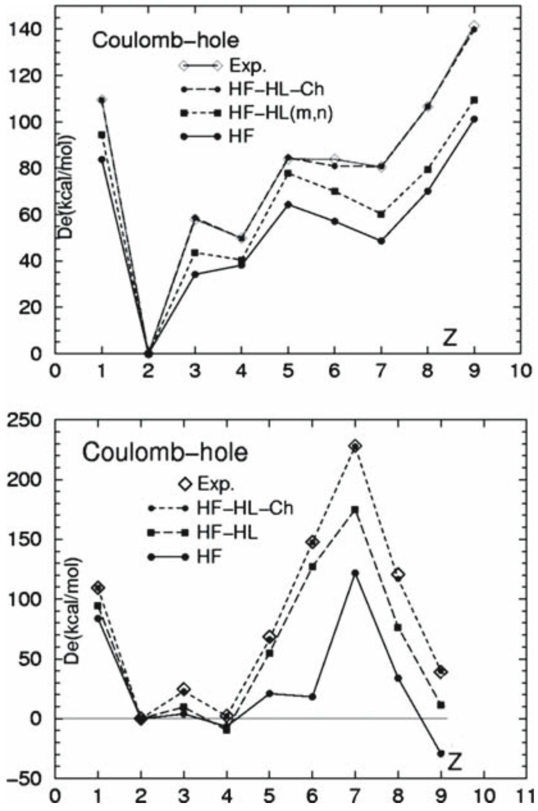

Fig. 4 *Top* Coulomb–hole [HF–HL–Ch] binding energy (kcal/mol) for hydrides compared with HF and first step HF–HL results. *Bottom* same for homopolar molecules

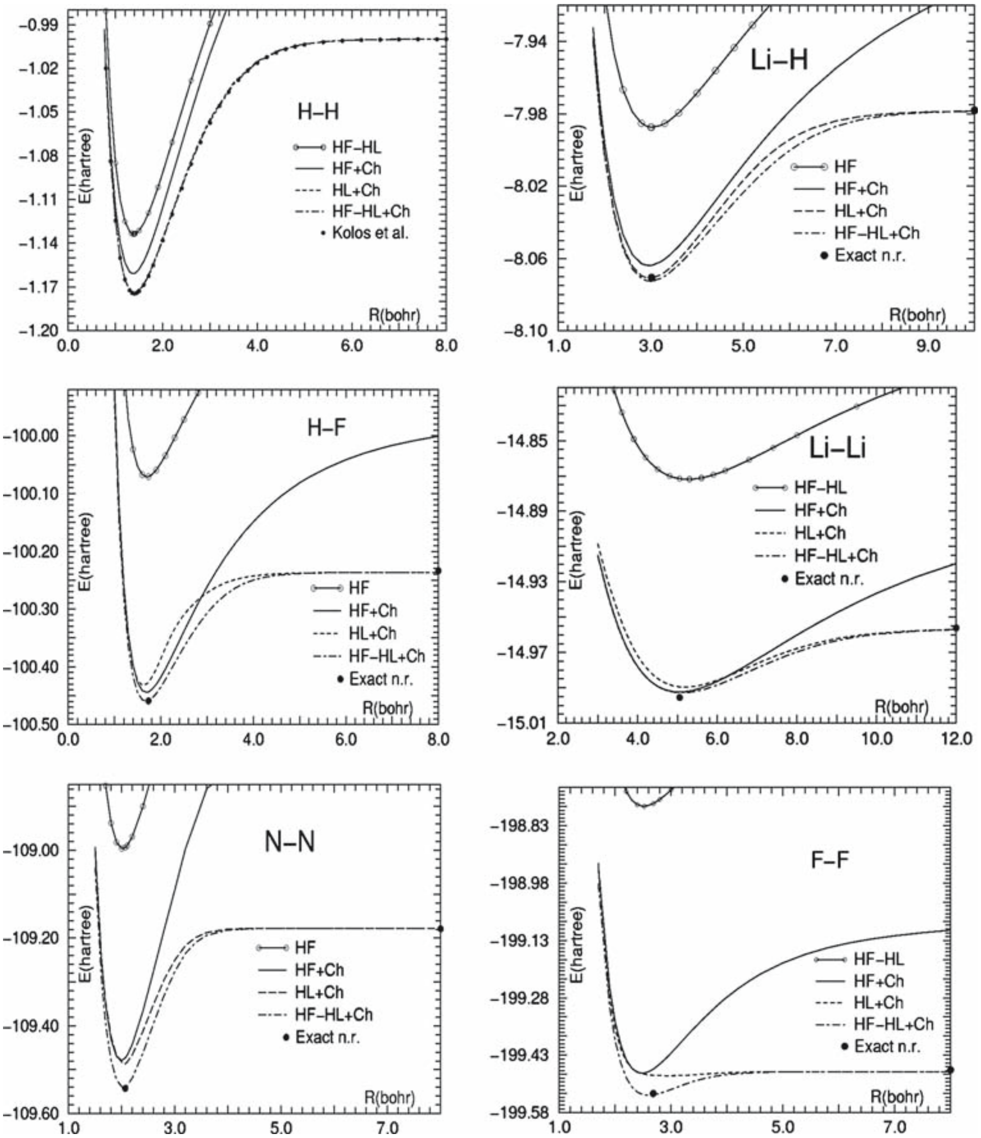

Fig. 5 Potential energy curves with Coulomb hole approximation from HF, HL, HF–HL computations for $H_2[^1\Sigma_g^+]$, BeH$[^2\Sigma^+]$, HF$[^1\Sigma^+]$, $Li_2[^1\Sigma_g^+]$, $N_2[^1\Sigma_g^+]$, and $F_2[^1\Sigma_g^+]$ compared with first step HF–HL potential energy curves and to non-relativistic exact energies at equilibrium and dissociation

The binding energy data obtained with the Coulomb hole DFA are displayed in Fig. 4 for the full set of hydrides (top inset) and homopolar molecules (bottom inset). To facilitate comparison we have added the experimental, the HF–HL first step and the HF binding energies. The agreement with experimental data is excellent, considering that the entire approach is condensed to a few ab initio configurations and a simple DFA correction.

In Fig. 5 we report potential energy curves for selected hydrides and homopolar molecules complementing Fig. 4. Note the overall accuracy but also the slight shift to short distances for HF, N_2 and F_2. In Refs. [70] and [71] we report the full set of computations of the first and second row hydrides and homopolar molecules. The H_2 computed HF–HL–Coulomb hole energies are accurate for the full range of internuclear separations including the highly repulsive region.

7 HF and HF–HL correlation energies

In general, to analyze the molecular binding energy we compare the equilibrium geometry total molecular energy with the sum of the ground state energies of the component atoms. However, if we use a quantum mechanical model, since the latter is only an approximation, we must also attempt to estimate the error of the approximation. It is therefore of interest to consider the correlation energy error in the HF and in the

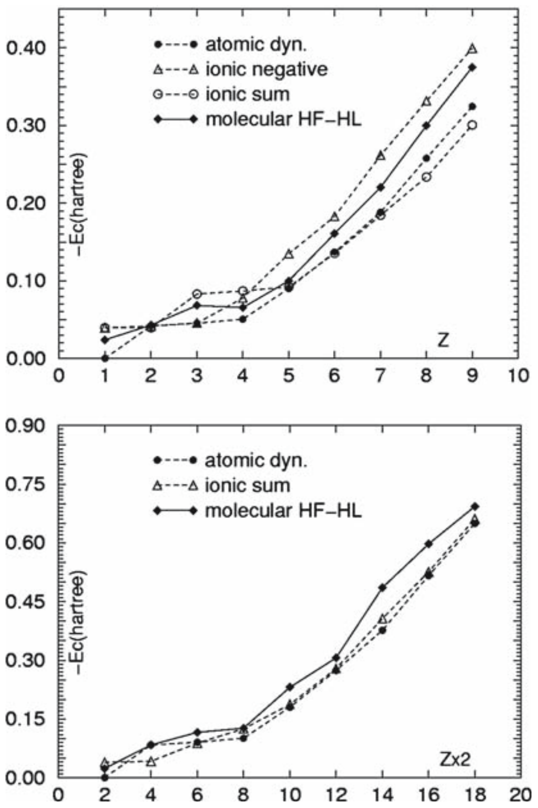

Fig. 6 Correlation energy from HF–HL computations compared with neutral atom and ion correlation energies corrected for near-degeneracy. *Top inset* for hydrides, *bottom inset* for homopolar molecules (see text)

HF–HL approximations. We know that the error has been reduced in HF–HL computations by the introduction of ionic configurations, the "ionic structures" in the VB language. This consideration brings about the desirability to consider the computed error not only for the separated neutral atoms but also for the combination of the separated positive and negative ions, participating to the ionic structure.

In Fig. 6 (top inset), we report for the hydrides the dynamical correlation energy resulting from the HF–HL computations, the sum of the dynamical correlation energies for the neutral atoms (for hydrides it is simply the atomic correlation for the atom X) and the sum of the dynamical correlation energies for the positive and negative ions forming the ionic structure.

We note that, since the HF–HL has accounted for the non-dynamical correlation, also the atomic and ionic data must be equally corrected by subtracting from the total correlation energy the non-dynamical component. Further, we note that the correlation energy for the ionic pair H^+X^- coincides with the correlation energy of X^-, whereas the correlation energy for the pair H^-X^+ is the sum of the correlation energy for H^- (0.03951, hartree) and for X^+.

The data in the top inset of Fig. 6 show that the three sets of correlation energies are, as expected, increasing with Z, following the pattern of the atomic correlation energies. The latter are often very close (non distinguishable in the graph), for example and as expected, for the He atom the atomic, the negative ion and ionic sum $He^+(^2S; 1s^1) + H^-(^1S; 1s^2)$ have essentially equal correlation energy, but this is also the case, due to near degeneracy, for $Li(^2S; 1s^22s^1)$ compared to $Li^-(^1S; 1s^22s^2)$, and for $B^+(^1S; 1s^22s^2) + H^-(^1S; 1s^2)$ compared to $B(^2P; 1s^22s^22p^1)$ and, equivalently for carbon and nitrogen. The close values of the negative ion $(X^- + H^+)$ with the molecular correlations for the C, N, O and F atoms and the close values for the ionic sum $(H^- + X^+)$ with the molecular correlation for Li, Be and B bring to mind the electro-negativity scale. Note in this regard the equidistance of the molecular correlation value from the negative and positive ionic correlations for the C atom. For the homopolar molecules (bottom inset) the diagrams are very different, with the molecular correlation larger than the ionic for $F_2, O_2, N_2, C_2, B_2, Li_2$, but not for Be_2 and H_2.

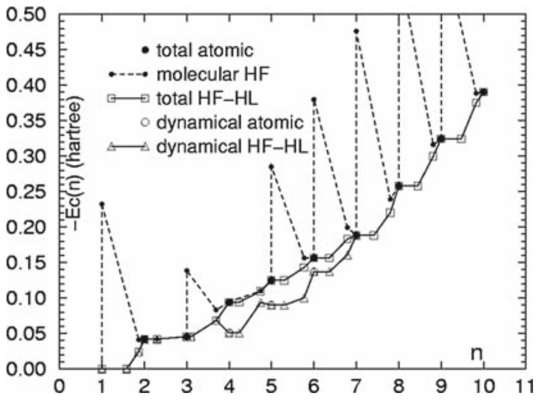

Fig. 7 Hydride correlation energy: atomic correlation, with and without near-degeneracy, compared with molecular HF and HF–HL correlations at the united atom, equilibrium and near dissociation (see text)

In Fig. 7 we analyze in detail the correlation energy of the diatomic hydrides HX. These molecules provide a unique example where the correlation energy of HX at the united atom is equal to the correlation of HX′ at dissociation for $Z(X') = 1 + Z(X)$. In this way, by considering the hydrides from H–H to H–F, we can analyze the smooth correlation energy variations in a system of electrons increasing from 2 to 10.

To achieve this, we report in the ordinate the $Ec(n)$ values and in the abscissa the number of the electrons n, either for the atom X' or for the hydride HX. In addition, we attribute to the abscissa a dual role, representing also internuclear distances. For a given HX(n) hydride, Ec(n) varies from the internuclear separation with R(HX)=0 bohr, plotted at the value n on the abscissa, to R(HX)=10 bohr made to correspond to $(n - 1)$ on the abscissa. Alternatively stated, each interval, n to $n - 1$, represents also the scaled internuclear separations from R(HX)=0 to R(HX)=10 bohr, the latter corresponding essentially to dissociation.

In Fig. 7 we plot the total HF atomic correlation energies without (full large bullet) and with (large circle) near-degeneracy considerations. In addition, for the hydrides we report the correlation energies $E_{\mathrm{c(HF)}}$ connected by a dashed line at the united atom, at equilibrium (small bullet) and at dissociation (small bullet), the total $E_{\mathrm{c(HF-HL)}}$ (square marks connected by a solid line) and the dynamical $E_{\mathrm{c(HF-HL)}}$ (triangle marks connected by a solid line). Thus, the HF molecular correlation at different internuclear separations is represented by the dashed pattern, whereas the HF–HL molecular correlation at different internuclear separations is represented by the full line patterns, one with inclusion of near degeneracy, the other (upper) without. The atomic correlation energy value for the atom with $Z = n$ is equal to the correlation energy of HX(n) at the united atom, R(HX)=0, both in the HF–HL and HF approximations. In addition, the atomic correlation energy value for the atom with $Z = (n-1)$ corresponds to the correlation energy of HX(n) at dissociation, $R(\mathrm{HX})=\infty$ in the HF–HL approximation, but not for the HF approximation, which breaks down approaching dissociation (exception made for BeH). The HF correlation energy increases sharply concomitant with the HF model breakdown; in the graph we have reported the HF correlation at the united atom, at the equilibrium internuclear distance and at R(HX)=10 bohr. The HF–HL correlation energy is reported at the united atom, at the equilibrium internuclear distance, at $R(\mathrm{HX}) = 3 \times Re$ and at R(HX)=10 bohr. Note that at about $R(\mathrm{HX}) = 3 \times Re$ the HF–HL correlation is essentially equal to its value at dissociation.

From the figure it is evident that the atomic correlation energy is the dominant component of the hydrides total molecular correlation, exception made for those hydrides with very few electrons. Note that the difference in spin multiplicity, comparing the HX molecule and the X atom for $n = 6$ (^{3}P and $^1\Sigma$) and $n = 7$ (^{4}S and $^2\pi$), appears to be rather unimportant, at least for the energy scale of the figure. The role of the molecular extra correlation in molecular binding is evident, but at the same time the overall graph shows that the HX systems are essentially perturbed atoms, especially for large values of n (this observation follows also from the data in Fig. 5). Finally, the graph clearly points out that the HF representation becomes physically meaningless shortly after equilibrium (approximately after $R(\mathrm{HX}) = 2\times Re$) up to dissociation, whereas the HF–HL representation is realistic from the united atom to dissociation. The HF–HL model emerges as the model of preference at any internuclear distance thus it is the "reference function" for molecular systems.

8 Genealogy of the HF–HL method

There are—by now—many approaches in quantum chemistry, and therefore for a new method it is not a trivial task to draw the genealogical tree, an occasion to recognize goals and also eventual drawbacks.

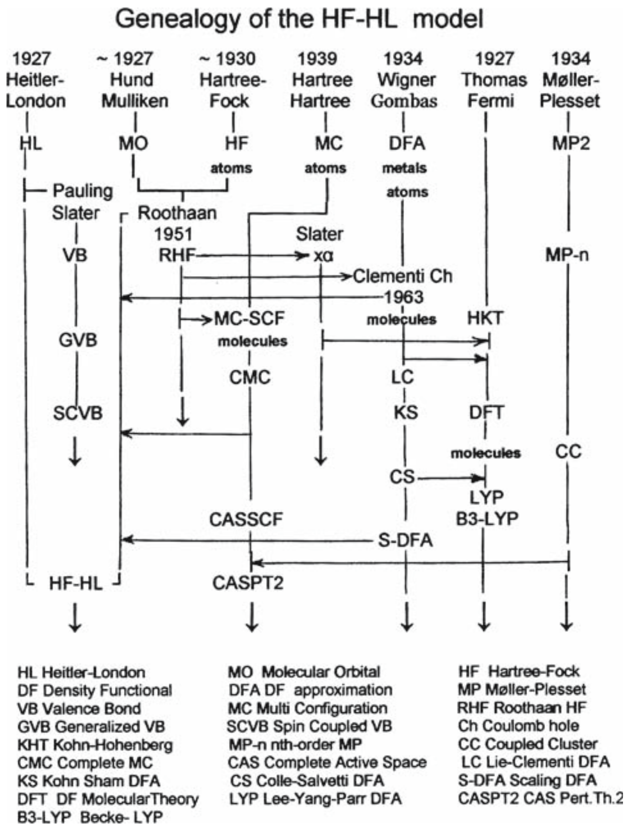

Fig. 8 Genealogy of the HF–HL method in the context of related atomic and molecular quantum mechanical models

In Fig. 8 we propose a genealogical tree for the HF–HL method in a simplified form. 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 eventual omissions.

At the top we list few of the starting seminal proposals relevant to the HF–HL method; this first line needs no comment. It remind us, however, that very little is really new —in a rigorous sense—in today computational chemistry: the new concepts date around the early 1930s, the computer implementations start (and often end) in the 1960s, with—all in all—modest improvements, often performed to keep up with the computer industry progress. Note that the academic recognition of pioneering ideas has been and is, all in all, uneven.

We are interested in the HF–HL method, given on the bottom of the figure, thus we cover the time interval from the 1920s to the first few years of the twenty first century. The HF–HL method is clearly linked both to the HL and to the Roothaan RHF roots. This leaves out techniques to deal with the correlation effects. The non-dynamical correlation of the HF–HL "first step" brings about a link to the MC–HF technique on the first line of the tree. The use of DFA, the coulomb hole in particular, leads to a link to DFA.

The HF–HL approach is intended not only for computations of ground state molecular functions and energies at equilibrium but also for excited states, and at any internuclear separation both for small and for large molecular systems. Recall that a short cut to computationally intensive (Hylleraas, CI, MC–SCF, MP2 and—we add—today CASSCF and coupled clusters computations) was proposed by Wigner [25] when the dynamical correlation error was approximately corrected with a functional of the electronic density. The message was "the HF techniques is a valid starting point—over 95% of the exact non relativistic energy—which can easily lead to a full agreement with the laboratory data simply by using functionals of the electronic HF density". The obvious corollary is that the above statement is *a fortiori* true if the HF function is replaced by a better (but formally related) wavefunction.

Recall that Wigner, who introduced and defined for first the term "correlation energy", named the approach "statistical approximation", since based on the probabilistic interpretation of the electronic density, an interpretation not fully accepted in the physicists community of the early 1930. His effort was followed not only in Europe [26–29] but also in USA for example by Pines [97,98], Gell-Mann [99], and Bruekner [100]. In today theoretical and computational chemistry there seems to be only a very weak trace of the above literature.

In the period of 1962–1963 in California, one of us (E.C.) inspired by Wigner, introduced an approximated Coulomb hole correction directly in the electron–electron interaction in a recently written SCF computer codes. Since the main theoretical frame remained the HF frame, and since the Coulomb hole correction was included in the Fock operator, there seemed no need to call the Slater determinant and the orbitals differently from what previously called. In the derivation of the integral matrix elements related to the Coulomb hole correction a semi-empirical parameterization was adopted (relating to the electronic density via the overlap integral variables). A lengthy review paper dealing with the emerging computational chemistry for atom and molecules, including Coulomb hole correction and relativistic correction, was written; by early February 1964 the work with the Hartree–Fock Coulomb–hole corrected wavefunction and energies for the atoms from He to Ar was accepted by the *IBM Journal of Research and Development* [30] but the publication was long delayed, since the appendix of the review is the very lengthy publication of Clementi's Tables of Atomic Functions [31] (later the tables were extended in the Atomic Tables by Clementi and Roetti [101]). The Coulomb hole proposal and results were also presented in 1964 at international [102,103] and local meetings (like at Brueckner's group in La Jolla, CA, USA). The message was that the correlation correction can be included as a correction to be performed at the same time we compute the HF wavefunction, leading not only to an accurate energy but also to a new easily obtained function.

Alternative to this approach are (a) the density functionals described in Gombas volumes, unknown in the early sixties to one of us (E.C.) and (b) the "Slater exchange" formulations, started as a pragmatic simplification for solid state computation, adopted for example in the atomic computation by Hermann and Skillman [43]. Slater's work made clear a complementary message, namely that variation in the exchange parameterization could lead to lower energy, which could be made to agree with exact energies [42]. We recall that also the $x\alpha$ approach, at times publicized the doom of the HF model, prompted one of us (E.C.) with an invitation to act constructively rather than destructively [104]. Clementi and Slater's approach are complementary: in the HF model the electrons have an exaggerated Coulomb repulsion, which can be corrected either by decreasing the Coulomb integrals or by increasing the exchange integrals.

To avoid semantic confusions, we have designated as "density functional approximation", DFA, Wigner's and Clementi‘s path attempting to estimate as closely as feasible the correlation energy via semi-empirical functionals in HF computations. In the past 40 years there were several new DFA proposals [56–59] some with the correlation corrections not limited to the electron–electron and the kinetic energy but extended also to the electron-nuclear interaction [41], or extending the DFA approach to relativistic functions [62] or, finally, not using HF wave functions but short MC–HF expansions [60,61]. A number of DFA density functionals tested and collected trough the early 1990s are documented in [105], and implemented in the HF–HL computer code.

Figure 8 deals with the origins of the HF–HL method, from the beginning of quantum chemistry with the MO and HL proposals up to the present time. Most likely there will be methodological extensions based on others "old" concepts like natural orbitals [106–109], NO, and different orbitals for different spins [110]. The HF–HL basic mathematical structure is the variational addition of two determinantal wave functions, the HF and the HL. However, the two determinants can be contracted into one yielding a new determinantal function, the "compact-HF–HL" wavefunction, C–HF–HL. Indeed, for example in a diatomic molecule AB, the space part of the molecular orbital can be constructed by a variational addition of a traditional MO (available from the HF component of the HF–HL function) and either the atomic orbital AO_A on atom A, or the atomic orbital AO_B on atom B (available from the HL component of the HF–HL function). For example in H_2, starting with the usual canonical MO, $1\sigma_g$, and the two canonical AOs, $1s_A$ and $1s_B$, one might attempt to construct a C–HF–HL wave function from the two new molecular orbitals $(c_1 1\sigma_g + c_2 1s_A)\alpha$ and $(c_1 1\sigma_g + c_2 1s_B)\beta$; the $1\sigma_g$, $1s_A$ and $1s_B$ can be obtained, as starting approximation, from the HF–HL optimized wavefunction with c_1 and c_2 are new variational coefficients.

Therefore, to the canonical HF molecular orbitals there correspond two non-orthogonal and different molecular orbitals, each one with its own spin function. In this way the C–HF–HL wavefunction would be constructed with "different orbitals for different spins", a well-known algorithm to introduce correlation corrections. Note that this construction explains also the gain obtained with the use of ionic structures. Indeed, the matrix elements for the C–HF–HL function include the equivalent of those derived for ionic structures in the HF–HL model. The build up principle for the C–HF–HL function can be taken directly from Herzberg's orbital diagrams [6], connecting the united atom orbital, to the molecular orbitals at equilibrium separation and to the atomic orbitals at dissociation.

9 Conclusions

We have discussed on a new variational computational method, the Hartree–Fock–Heitler–London, and compared Hartree–Fock, Heitler–London, and Hartree–Fock–Heitler–London potential energy curves for the first and second period hydrides and homonuclear molecules. We recall that neither the HF nor the HL approximation are capable of systematically reproducing, at least qualitatively, the basic molecular binding features known experimentally (bond breaking and bond formation). Further, the HF model breaks down at dissociation preventing any assessment of the correlation correction for internuclear separations larger than about twice the equilibrium distance. The two traditional methods, however, have the high merits of mathematical simplicity and immediate physical interpretability, and, because of these two basic qualities, have historically provided two distinct and competing quantum chemical "reference" wavefunctions for theoretical and computational chemistry and are at the origin of the most basic concepts in physical chemistry and in chemical physics.

The HF-HL method variationally merges the two historical paths, at a marginal increase in computational complexity, retaining at the same time the physical interpretability of the two original contributions. The combination of the two methods into the HF–HL approach eliminates grossly unphysical approximations, particularly at large internuclear separations, accounts for non-dynamical correlation and state crossing and predicts molecular binding more reliably.

The post-HF–HL is carried out either ab initio or within the density functional approximations, DFA. For few electron diatomic molecules, H_2, HeH, LiH, and BeH, we have computed ab initio the total correlation with rather extended MC–HF and MC–HL expansions leading to good agreement with experimental binding and total non- relativistic energies. More importantly, however, we have shown for the first and second period diatomic hydrides and homopolar molecules, that the molecular extra correlation energy can be essentially accounted for with the computation of only a few HF–HL ab initio configurations, thus yielding very reasonable binding energies.

The post-HF–HL computations with DFA, for example with the Coulomb hole functional, yield in a simple way accurate molecular binding and total energies, both at equilibrium and at dissociation. Work is in progress to test a variety of different density functionals [70,71].

In summary, the HF–HL approach provides (1) a reliable "zero-order reference wavefunction" while maintaining mathematical simplicity and immediate physical interpretability, (2) the computation of the molecular extra correlation energy points to the possibility to obtain ab initio very reasonable binding energies with much shorter expansions than today general assumed, (3) the computation with DFA of post-HF–HL functions and energies remains a pragmatic answer for large chemical systems, (4) since the ab initio HF–HL method can account for an increasingly large fraction of the dynamical correlation, we expect that eventually the DFA approach will become a simple numerical list of empirical rules for numerical corrections of the smaller and smaller errors present in the ab initio functions.

We are now planning to extend the HF–HL approach to polyatomic systems, where likely the main drawback will be not the computation of the dynamical correlation but rather the optimization of the HL component; availability of Slater four center integral codes [111], will allow to replace the Gaussian basis sets and simplify the optimization effort.

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Appendix: Comment on the Coulomb hole and electron pairs

As we all know, the computation of the non-relativistic electronic correlation energy, E_c, is the aim of any post-Hartree–Fock approach. In this appendix, we recall early considerations, which relate the Coulomb hole approximation, the HF model and the exact non-relativistic energies. To start with, the relations between the exact non-relativistic energy and the HF energy can be elucidated (considering for simplicity closed shell structures) by writing

$$E_{HF} = \Sigma \mathrm{h_i} + \Sigma_\mathrm{i} \Sigma_\mathrm{j} (2\mathrm{J_{ij}} - \mathrm{K_{ij}}) \quad (1A)$$

$$E_{exact} = \Sigma \mathrm{h_i} + \Sigma_\mathrm{i} \Sigma_\mathrm{j} (2\mathrm{J_{ij}} - \mathrm{K_{ij}}) + E_c \quad (2A)$$

with both equations obeying the virial theorem. To explicitly connect Eqs. 1A and 2A, the correlation energy, E_c, a relatively small perturbation, can be represented as a term by term correction for the HF energy components in Eq. 1A; therefore we write the correlation energy as

$$E_c = \Sigma_i \Delta h_i + \Sigma_i \Sigma_j (2\Delta J_{ij} - \Delta K_{ij}) \quad (3A)$$

yielding

$$E_{exact} = \Sigma_i \mathbf{h}_i + \Sigma_i \Sigma_j (2\mathbf{J}_{ij} - \mathbf{K}_{ij}) \quad (4A)$$

with

$$\mathbf{h}_i = h_i + \Delta h_i \quad (5A)$$

$$\mathbf{J}_{ij} = J_{ji} + \Delta J_{ij} \quad (6A)$$

$$\mathbf{K}_{ij} = K_{ij} + \Delta K_{ij} \quad (7A)$$

In this way the exact electronic energy, Eq. 4A, retains the structure of the HF energy expression, with corrections in each one of the HF terms [41]. Clearly, there is no problem in defining an exchange energy, since the overall framework is spin dependent and follows the HF model. With the Coulomb hole we correct the electron–electron interactions, as shown in Eqs. 6A and 7A; due to the SCF algorithm this brings about new spin–orbitals (different from the HF orbitals) leading also to Eq. 5A. The potential energy curves and the binding energies in Figs. 4 and 5 are once more a gratifying verification of this approach.

Eq. 3A can be formally re-written by collecting terms depending on one orbital and those on two orbitals, namely inter- and intra-pair correlation energies:

$$E_c = \Sigma_j e_{ii} + \Sigma_i \Sigma_{j \neq i} e_{ij} \quad (8A)$$

This equation reminds us of Eq. 7 in Sect. 3.1, with a decomposition among atoms rather than among orbitals. These two different, but equivalent, decompositions are once more consequences of the two view points, MO for Eq. 8A and VB for Eq. 7. Stressing the VB perspective with Eq. 7 we are lead to "structures", stressing the MO picture with Eq. 8A we are lead to configuration mixing.

The Coulomb hole proposal and its application to atomic systems [30,32–34] are the first quantum chemistry example where E_{exact} is approximated via modified HF matrix elements yielding the "Clementi orbitals". Extending Wigner's concept, related to a radius r_s(i) for electron i with spin up, delimiting a space region impermeable to electron j with spin down and its associated radius r_s(j), the Ch functional [30] modifies the standard Hartree–Fock 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) and r(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 semi-empirical parameter density dependent, approximating the coulomb hole [30]. The new Coulomb interaction matrix element is therefore computed as

$$\int_0^\infty f(i) \left[\int_0^{r_a} f'(j) dr(j) + \int_{r_b}^\infty f''(j) dr(j) \right] dr(i) \quad (9A)$$

where $f(i)$, $f'(j)$, $f''(j)$ are standard expressions related to the orbital basis set representation for electrons i and j, respectively. Note that the above integration over the radial part of the basis set functions is performed independently from the integration over the orbital angular part, thus δ must be parameterized for specific combinations of s, p, d, f, ... functions. The above cut off is "hard", thus the expression in Eq. 9A is designated as the "hard Coulomb hole".

Later the original "hard Coulomb hole" was modified into "a soft Coulomb hole" [56] by replacing the Coulomb operator $[1/r_{ij}]$ with the operator $\left[1 - \exp(-\alpha r_{ij}^2)\right]/r_{ij}$. The value of α, a semi-empirical density dependent value, is determined by fitting atomic energies and ionization potentials for specific combinations of s, p, d, f, ... functions.

In the Ch functional the dependency on the electronic density is indirect since the parameters for δ or α are fitted using the variables present in the basis set (namely, orbital exponents, angular symmetry and overlap of the basis functions). However, the obtained parameterization has been proved to be essentially basis set independent [58], particularly for large basis sets; indeed it hardly would makes sense to compute post-HF energies with basis set not adequate to yield energies of near-HF limit quality.

Next, recalling Hylleraas [112], we note that the old stumbling block, namely the availability of many-center many-electron integrals has been partially removed [113, 114], allowing progress toward many electron system computations. However, the proposal cannot be realistically considered for large molecular systems. In this context, we note that the soft Coulomb hole functional correction [56, 58] is related to Hylleraas proposal. Indeed, since the soft Coulomb hole correction replaces the $1/r_{12}$ operator with one of the form $F = \left[1 - \exp(-\alpha r_{12}^2)\right]/r_{12}$ the corresponding Coulomb matrix elements over orbitals φ are:

$$\langle \varphi_i(1)\varphi_j(2)|F|\varphi_k(1)\varphi_l(2)\rangle = J_{ijkl} - J'_{ijkl}, \quad (10A)$$

with

$$J_{ijkl} = \langle \varphi_i(1)\varphi_j(2)|1/r_{12}|\varphi_k(1)\varphi_l(2)\rangle \quad (11A)$$

$$J'_{ijkl} = \left\langle \varphi_i(1)\varphi_j(2)|\exp - (\alpha r_{12}^2)/r_{12}|\varphi_k(1)\varphi_l(2)\right\rangle \quad (12A)$$

with α semi-empirical parameter density related. Note that Eq. 12A can lead to quantities like

$$\langle \exp-(\alpha' r_{12})(\varphi_i(1)\varphi_j(2)|1/r_{12}|(\varphi_k(1)\varphi_l(2)\exp - (\alpha' r_{12})\rangle \quad (13A)$$

namely, a Hylleraas-type term. The analytical expression for the computation of the integrals of Eq. 13A are available in [115].

Note added in proof: The HF-HL computer code, written by one of us (GC) and summarized in Sect. 2.1, is presently extended by including gradient techniques for the optimization of the coefficients of the orbital expansions. In addition, the new version of the code has the option to use either Gaussian or Slater-type functions. These extensive modifications have been made during a stay at the Universidad Autonoma of Madrid, Spain, in the Department of Chemistry under the guidance of Prof. Jaime Fernandez Rico.

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