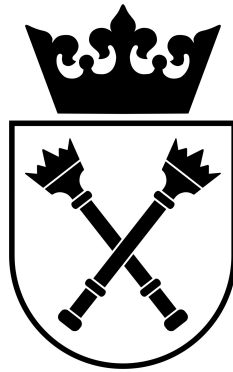


Uniwersytet Jagielloński
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Rozprawa doktorska



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Strong Correlations in Molecular Systems: True Covalency and Atomicity

Promotor: prof. dr hab. Józef Spalek
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Serdeczne podziękowania kieruję do promotora tej pracy prof. Józefa Spalka za opiekę merytoryczną oraz ciągłą gotowość do dyskusji o dowolnej porze podczas przygotowania niniejszej pracy oraz całego kształcenia w szkole doktorskiej.

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Ja niżej podpisany Maciej Hendzel (nr indeksu: 1103575) doktorant w Szkole Doktorskiej Nauk Ścisłych i Przyrodniczych Uniwersytetu Jagiellońskiego oświadczam, że przedłożona przeze mnie rozprawa doktorska pt. „Strong Correlations in Molecular Systems: True Covalency and Atomicity” jest oryginalna i przedstawia wyniki badań wykonanych przeze mnie osobiście, pod kierunkiem prof. dr hab. Józefa Spałka. Pracę napisałem samodzielnie.

Oświadczam, że moja rozprawa doktorska została opracowana zgodnie z Ustawą o prawie autorskim i prawach pokrewnych z dnia 4 lutego 1994 r. (Dziennik Ustaw 1994 nr 24 poz. 83 wraz z późniejszymi zmianami).

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Kraków, dn. 7.06.2024

Podpis autora

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Publications/preprints constituting this Thesis

Published papers

1. **M. Hendzel**, M. Fidrysiak, J. Spalek, Many-particle covalency, ionicity, and atomicity revisited for a few simple example molecules, *Journal of Physics B: Atomic, Molecular and Optical Physics* **55**, 185101 (2022).
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4. E. Broclawik, M. Fidrysiak, **M. Hendzel**, J. Spalek, Interparticle correlations and chemical bonding from physical side : covalency vs atomicity and ionicity, (M. Musiał and I. Grabowski, Eds.), *Advances in Quantum Chemistry: Polish quantum chemistry from Kołos to now*, Academic Press, pp. 351-373 (2023).

Submitted preprints

1. J. Spalek and **M. Hendzel**, Exact entanglement correlations as an attribute of chemical bond, arXiv:2406.06171 (2024).
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Abstract

This Thesis aims to examine diatomic molecular systems using method (EDABI) developed and applied in our group and subsequently applied to systems with strongly correlated electrons. In this manner we contribute to the ongoing discussion on the fundamentals of quantum chemistry, particularly chemical bonding and the basic quantum mechanical aspects, especially the entanglement of two fermions. Explicitly, we introduce the concepts of true covalency and atomicity and discuss their role in the complementary characterization of chemical bonds. The diatomic molecular systems studied are H_2 , HeH^+ , LiH , chH_2^+ , and H_2^- . The thesis starts with the exact solution of the extended Heitler-London model for H_2 molecule and addresses next the dynamic interplay between the true covalency, atomicity and ionicity. Furthermore, we analyze the dynamic contributions to the ground state energy, coming from all single-particle and interaction terms. We highlight the correspondence between behavior of molecular systems and nanosystems at the Mott-Hubbard localization threshold. The work involves also a comparative analysis of results obtained from the EDABI method with those from other state-of-the-art quantum-chemical methods, such as Configuration Interaction (CI) and Hartree-Fock (HF) methods. Finally, we relate the new characteristics introduced earlier to the entanglement correlation, as exemplified by the von Neumann entropy.

Keywords: hydrogen molecule, two-atom molecular systems, strong correlations in molecules, true covalency, atomicity, Mott-Hubbard phenomenon in bonding

Streszczenie

Niniejsza praca doktorska ma na celu zbadanie dwuatomowych układów molekularny przy pomocy metody (EDABI) opracowanej i stosowanej w naszym zespole, a następnie zastosowanie jej do układów silnie skorelowanych elektronów. W ten sposób przyczyniamy się do trwającej dyskusji na temat podstaw chemii kwantowej, w szczególności wiązań chemicznych i podstawowych aspektów mechaniki kwantowej, zwłaszcza splątania dwóch fermionów. Wprowadzamy pojęcia kowalencyjności właściwej i atomowości oraz omawiamy ich rolę w komplementarnej charakterystyce wiązań chemicznych. Badane dwuatomowe układy molekularne to H_2 , HeH^+ , LiH , H_2^+ oraz H_2^- . Praca rozpoczyna się od dokładnego rozwiązania rozszerzonego modelu Heitlera-Londona dla H_2 a następnie skupia się dynamiczną interakcją między kowalencyjnością właściwą, atomowością i jonowością. Ponadto, analizujemy dynamiczne wkłady do energii stanu podstawowego, pochodzące ze wszystkich jednocząstkowych i dwucząstkowych składników. Podkreślono związek między zachowaniem się układów molekularnych a układów nano na progu lokalizacji Mott-Hubbarda. Praca obejmuje również porównawczą analizę wyników uzyskanych metodą EDABI z wynikami innych nowoczesnych metod chemii kwantowej, takich jak metoda konfiguracji oddziaływań (CI), czy metoda Hartree-Focka (HF). W końcu odnosimy wprowadzone przez nas charakterystyki do korelacji splątania wyrażając je poprzez entropię von Neumanna.

Słowa Kluczowe: molekula wodoru, dwuatomowe układy molekularne, silne korelacje w molekułach, kowalencyjność właściwa, atomowość, zjawisko Motta-Hubbarda w wiązaniu

List of abbreviations and symbols

Frequently used abbreviations

- EDABI - Exact Diagonalization Ab Initio,
- MO - Molecular Orbitals,
- VB - Valence Bond,
- HL - Heitler-London,
- HF - Hartree-Fock,
- M-H - Mott-Hubbard boundary

Frequently used symbols

- γ_{cov} - covalency
- γ_{ion} - ionicity,
- γ_{at} - atomicity,
- γ_{bond} - bonding,
- S - von Neumann entropy,
- ϵ - atomic energy magnitude,
- t - hopping energy magnitude,
- U - Hubbard intraatomic interaction parameter,
- K - interatomic interaction parameter,
- V - correlated hopping parameter,
- J - Heisenberg spin-exchange integral,
- ρ - electron density

Chapter 1

Aim and scope of the thesis

The aim of this doctoral thesis is to investigate diatomic molecular systems using methods developed in our group and applied to systems with strongly correlated electrons. This approach contributes to the ongoing discussion on the fundamentals of the quantum chemistry, i.e., chemical bonding, and the basics of quantum mechanics, i.e., the entanglement of two fermions. A significant focus is placed on the new concepts of true covalency and atomicity, and their roles in characterizing of the chemical bond.

The scope of this work includes the numerical implementation of the Ab Initio Exact Diagonalization (EDABI) method, based on the combined language of first and second quantization and applied to finite diatomic molecular systems (H_2 , HeH^+ , LiH , H_2^+ , H_2^-). This thesis also encompasses the analysis and interpretation of the characteristics of chemical bonding based on the first exact solution of the Heitler-London (Mulliken) model for the H_2 molecule, focusing particularly on the dynamic interplay of true covalency, atomicity, and ionicity.

Furthermore, the dissertation explores the dynamic contributions to the ground state energy from all two-particle interactions, as a function of interatomic distance. The research highlights the correspondence between the behavior of molecular systems and larger systems at the Mott-Hubbard onset, emphasizing how the principles derived from more complex nanosystems and bulk systems can help in studying and understanding of diatomic molecular systems.

Additionally, the work involves a comparative analysis of results obtained from the EDABI method with those from state-of-the-art quantum chemistry methods, such as Configuration Interaction (CI) and Hartree-Fock (HF) methods.

Through these investigations, this dissertation aims to provide a deeper understanding of the fundamental properties of chemical bonds in molecular systems, bridging the gap between molecular physics and condensed matter physics, and offering new insights into the true covalency, atomicity, and ionicity of chemical bonds.

Chapter 2

Introduction

2.1 Molecular systems as nanosystems

In this subsection, we aim to situate our research within the broader context of our group studies using the EDABI method. The first applications of the EDABI method were related to nanosystems, such as hydrogen chains and clusters [1, 2, 3]. The method proved effective in determining the ground state energy and properties of those systems. One of the most significant achievements using the method was a detailed study of the particle quasi-momentum distribution $n_{k\sigma}$ (where k is the quasi-momentum and σ is the spin-quantum number) in the ground state for systems with one electron per atom. In particular, the research showed a universal character of the statistical distribution depending on the boundary conditions (periodic and antiperiodic). The results revealed that for an interatomic distance $R/a_0 \simeq 2.0$, the distributions resemble a modified Fermi-Dirac function, indicative of Fermi liquid behavior even for short chains and rings. However, as R/a_0 approaches 5, the distribution becomes continuous, showing a crossover transition from Fermi-liquid-like behavior to atomic-like states. This evolution is crucial for understanding the crossover from delocalized to localized states in nanosystems. This behavior reflects the unique properties of correlated nanoscopic systems, which differ from bulk systems. The concept of Hubbard subbands was introduced to nanoclusters, corresponding to the HOMO–LUMO splitting (i.e., the gap between the highest occupied and lower unoccupied state) in molecular and organic solid systems. The appearance of these subbands indicates the presence of magnetic-like splitting (Slater-like), even without explicit symmetry breaking, and is due to extended spin-spin correlation functions extending over the entire nanosystem.

The series of the former studies on hydrogen systems [4, 3, 5] concluded with research on the potential metallization of hydrogen and the transition between molecular and atomic (Mott-type) phases in hydrogen-cluster systems. Additionally, the method was successfully applied to dot-ring systems, where, beyond investigating the physical properties of the system, the contribution of three-node integrals to the ground state energy was examined, which proved to be very significant for nanoscale systems.

In this context, we have used the EDABI method to calculate the ground state energy of LiH and LiH·H₂ clusters, which are indicated as potential candidates for hydrogen storage. Fig. 2.1 illustrates the dependence of the ground state energy of those systems on the cell volume fitted to the Birch-Murnaghan Equation of State [6]. This example can be used also potentially as potentially extending our research to more complex situations.

The research in this Thesis complements the series of studies previously conducted

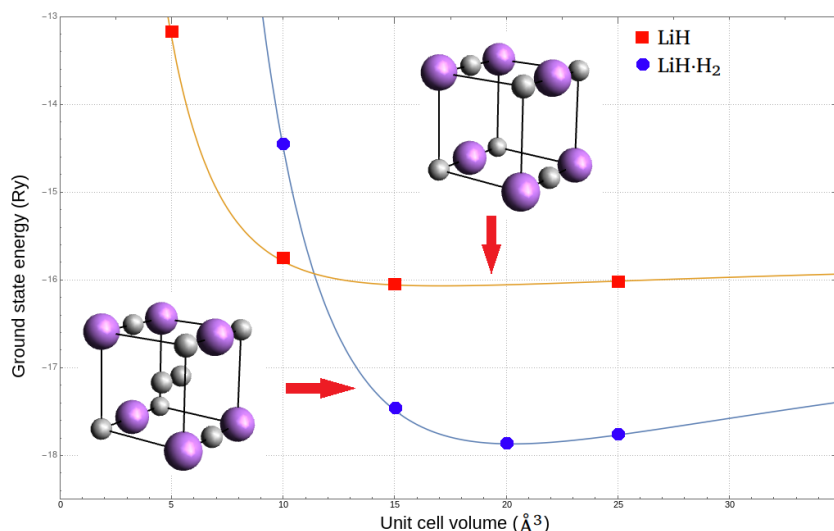


Figure 2.1: Total energy for LiH (squares) and $\text{LiH} \times \text{H}_2$ clusters as a function of unit cell volume as obtained from EDABI [M. Hendzel, unpublished].

in our group. Namely, it examines the fundamental properties of chemical bonding for diatomic molecules treated as two-site nanoscopic systems. However, it supplements it with new fundamental characteristics of the bonding, as detailed below.

2.2 The chemical bonding

There is one question about chemical bonding that remains prevalent in the literature, despite significant progress in quantum chemistry: why do neutral atoms bind? This question is not the only one that can be asked. It merely serves as a pretext for posing many other questions, such as those about the types of chemical bonds, the characteristics of chemical bonds, and so on.

Figure 2.2 illustrates the key milestones in the evolution of chemical bonding theories. In 1916, G. N. Lewis’s proposal of the bonding theory marked a revolutionary step by introducing electron pairs as a fundamental concept in chemical bonds [7]. This idea laid the groundwork for understanding how atoms share electrons to form stable molecules, represented through the so-called Lewis structures or electron dot diagrams.

In 1927 W. Heitler and F. London pioneered the application of quantum mechanics to chemical bonding, particularly elucidating the nature of the hydrogen molecule. Their work demonstrated how the Schrödinger equation could be employed to describe electron interactions within molecules, setting the stage for the quantum theory of bonding [8].

By 1931, the field had progressed significantly with R. S. Mulliken and F. Hund’s formulation of Molecular Orbital (MO) theory [9, 10]. This theory provided a framework for describing electron distribution across a molecule. Concurrently, L. Pauling introduced the hybridization concept, which offered insights into molecules’ shapes and bond angles by forming hybrid orbitals from atomic states. Pauling’s contributions also encompassed the Valence Bond (VB) theory, enhancing the understanding of molecular geometry [11].

The 1960s brought further advancements with K. Fukui and R. B. Woodward’s development of the frontier MO theory [12, 13]. This approach linked chemical reactivity

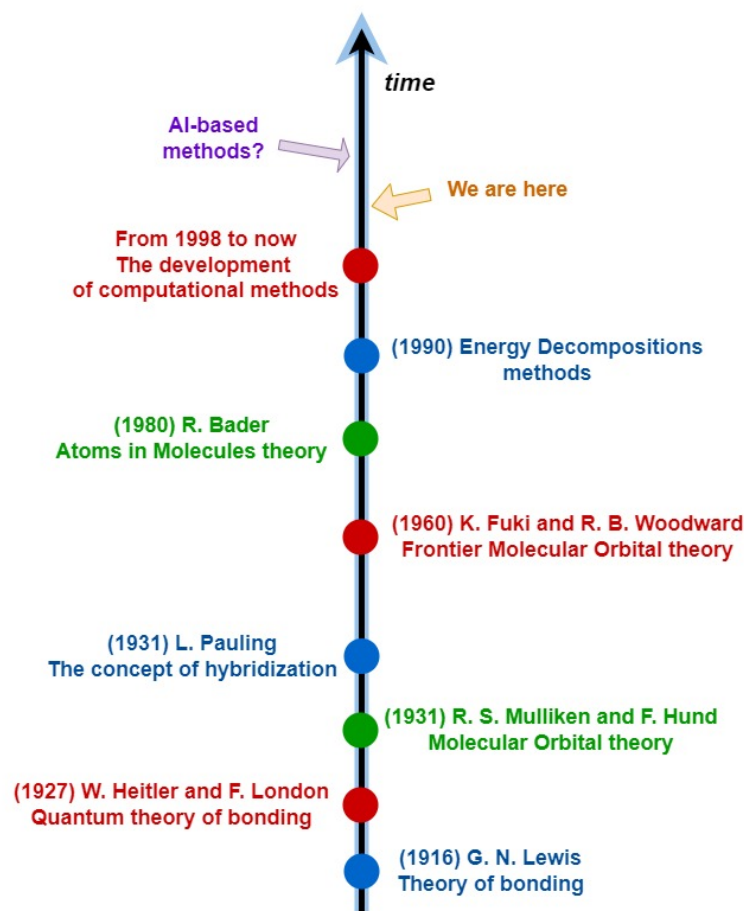


Figure 2.2: The timeline illustrating subjective selection of the key milestones in the development of theories related to chemical bonding.

to interactions between the Highest Occupied Molecular Orbital (HOMO) and the lowest Unoccupied Molecular Orbital (LUMO), providing a predictive tool for reaction mechanisms and earning both scientists the Nobel Prize in Chemistry in 1981.

By 1980 R. Bader’s Atoms in Molecules (AIM) theory emerged as a novel approach to analyzing electron density within molecules [14]. AIM formulation make use of the topology of electron density and defining of atomic boundaries and describing bonding interactions.

The 1990s witnessed the emergence of energy decomposition methods, which enabled the dissection of binding energies into individual components such as electrostatic, orbital, and steric interactions [15, 16, 17, 18]. These methods provided a deeper insights into the forces stabilizing chemical bonds.

The subsequent decades have continued to see significant advancements, notably the introduction, as well as, widespread adoption of density functional theory (DFT) in the mid-20th century. The contributions of Walter Kohn and Lu Jeu Sham and John Pople (later) in developing DFT revolutionized computational chemistry, offering a practical and efficient method for studying electronic structures of large molecules. DFT’s balance of accuracy and computational feasibility has made it a cornerstone in theoretical quantum chemistry.

Moreover, the integration of advanced spectroscopic techniques and high-performance computing has further refined our understanding of chemical bonding. These advance-

ments have allowed for more precise investigations into molecular interactions and dynamics, continually expanding the boundaries of chemical bonding theories and their applications in various scientific disciplines.

There are various methods of categorizing chemical bonds based on their physical properties, chemical activity, and other factors. One method originates from G. N. Lewis, mentioned earlier, is the concept of ionic and covalent bonding. Lewis’s seminal 1916 paper “The Atom and the Molecule” [7] laid the foundation for understanding chemical bonds in terms of shared electron pairs (covalent bonding) and the transfer of electrons (ionic bonding), thereby introducing the electron pair theory and the octet rule. However, the classification into covalent and ionic bonds remained a heuristic principle for a long time.

Linus Pauling was the first to introduce a numerical definition of ionicity in his influential book entitled “The Nature of the Chemical Bond” in 1932 [11]. Pauling proposed measuring ionicity by calculating the difference in electronegativity between the constituent atoms of a bond. He suggested that larger differences in electronegativity indicated more ionic bonds, whereas smaller differences indicated more covalent bonds. In these terms, any homoatomic chemical bond is purely covalent.

The molecular wavefunction first appears as a combination of the so-called covalent-wavefunction and ionic-wavefunctions in the work of R. Mulliken [9] from 1932, which was a continuation of the approach presented in the work of Heitler and London. This laid the foundation for understanding the dual nature of chemical bonds, integrating both covalent and ionic characteristics into a comprehensive quantum-mechanical framework. Both Heitler and London, as well as Mulliken, employed an ansatz to define the molecular wavefunction in a specific form. This particular form of the wavefunction, despite the different approaches, will be of paramount importance for the research findings presented in this dissertation.

In the realm of quantum mechanics, the initial understanding of chemical bonds was primarily based on electrostatic interactions, in accordance with the virial theorem. This theorem states that for a negative bonding energy (E), the electron potential energy (V) decreases by $V = 2E$, which is twice the increase in electron kinetic energy T . This model is supported by the observation that electrons tend to accumulate in the region between nuclei, creating an increased charge density compared to that of isolated atoms.

However, Ruedenberg’s research provided a deeper quantum mechanical explanation for bonding, especially in hydrogen atoms and molecules H and H_2 [19]. He demonstrated that approximately 66% of the bonding energy is due to constructive quantum interference that reduces the kinetic energy. This interference leads to delocalization of electron wavefunctions across both atomic centres, which is energetically more favorable than confinement within individual atomic orbitals. This delocalization results in a deviation from the simple virial theorem balance, causing the orbitals to contract towards the nuclei. In effect the potential energy slightly increases while the kinetic energy decreases. Such a phenomenon is easily observed by examining the optimization of spherical hydrogen 1s orbitals at various bond lengths.

This debate concerning the nature of chemical bonding, the origins of its covalency and ionicity, and the methods of defining them, did not conclude in the last century. Even up to the present year, numerous studies have attempted to explain the fascinating phenomenon of chemical bonding. Several contemporary works continue investigating bonding in terms of the competition between different kinds of component energies [20, 21]. It should be mentioned here that such methods have a significant drawback related to the dependence

of the results on the numerical method chosen for. What was elaborated in the most recent papers [22, 23]. Other works focus on topological aspects of the wave function and electronic density [24, 25]. Even such an approach is strongly dependent on the particular method used to divide density in real space. Some researchers are proposing a new kind of bonding beyond the standard division into covalent and ionic parts, such as in this paper where the charge-shift bond is postulated [26].

There is also one paper which contests the simple picture of the origin of covalent bonds given by Ruedenberg, as insufficient for a complete description of chemical bonding in various types of molecules [27]. As will be shown in the following chapters, our unequivocal analysis of the dynamic contribution of individual interactions to the total energy confirms the complexity of this phenomenon.

In the context of the works present in the literature, our contribution should be understood as an addition to the understanding of chemical bonding in molecules and an analogous to those in nanosystems and solids. We postulate the presence of residual atomicity in chemical bonding, as in fact, the molecular wave function is composed of the atomic functions. The classical understanding of covalency as the contribution from the covalent part of the wave function leads to the paradox of maximum covalency in the limit of the separated atoms. Studying the behavior of a molecular system as it gradually transforms to an atomic system led us to relate this behavior to Mott-Hubbard phenomenon. In the case of the exact solution of the hydrogen molecule, it agrees with the concept of atomicity in the bonding, which is the subject of this thesis.

Chapter 3

EDABI method: Exact analysis of the two-atomic molecular systems

3.1 First and second quantization combined

The method, on which this thesis dissertation is based, was developed relatively recently, is called **Exact Diagonalization Ab Initio** (EDABI) [1, 2]. This combines two components that are commonly used as separate quantum-mechanical methods. The first involves the Exact Diagonalization (ED) where the Hamiltonian in the second quantized form is diagonalized, either analytically or numerically [28]. The second pertains to first-principles calculations, known as ab initio approach [29]. The latter are also typically referred to as wave function methods, since they rely on representing various electronic states through linear combinations of Slater determinants. These determinants correspond to configurations where electrons are distributed differently across a set of one-electron orbitals.

A crucial aspect emerges at this point. If we contrast the wave function-based picture with the Hamiltonian picture in second quantization, where the latter is based on states constructed from creation and annihilation operators, we realize that we are essentially comparing two complementary pictures: the wave picture and the particle picture (or wave and particle formalism). In the literature one can find research grounded in either first- or second- quantization approach. Our strategy is different. In our works, describing and interpreting interesting features and properties of molecular systems are possible by the combination of these two languages.

Certain advantages of our approach also emerge for some specific systems, where it becomes possible to perform calculations in a mathematically rigorous manner. This is exemplified by the H_2^+ , H_2 , and H_2^- molecular systems, where only orbital size optimization was carried out within the numerical approach, primarily for practical reasons.

Figure 3.1 illustrates the flowchart of the method, highlighting the stages based on the formalisms of first and second quantization, respectively. As with any molecular calculations, the process begins by defining the system's geometry, as well as, requires the construction of an atomic basis set in order to define the field operators. The natural choice for the atomic basis set is that of Slater function [30]. Here are three exemplary

Slater wavefunctions for $1s$, $2s$ and $2p_x$, respectively,

$$\psi_{1s}(\mathbf{r}) = \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} e^{-\alpha|\mathbf{r}|}, \quad (3.1)$$

$$\psi_{2s}(\mathbf{r}) = \left(\frac{\alpha^5}{32\pi}\right)^{\frac{1}{2}} r e^{-\alpha|\mathbf{r}|}, \quad (3.2)$$

$$\psi_{2p_x}(\mathbf{r}) = \left(\frac{\alpha^5}{32\pi}\right)^{\frac{1}{2}} x e^{-\alpha|\mathbf{r}|}, \quad (3.3)$$

where α is a parameter commonly known as inverse orbitals size. However, as it is well-documented in the literature, the mathematical form of these functions makes them cumbersome for numerical applications [31]. Gaussian functions, on the other hand, are well-suited for numerical applications and can approximate Slater functions through contraction, which was written below

$$\psi_{1s}(\mathbf{r}) \approx \sum_i c_i e^{-\alpha_i |\mathbf{r}|^2}, \quad (3.4)$$

$$\psi_{2s}(\mathbf{r}) \approx \sum_i c_i (r - \beta_i) e^{-\alpha_i |\mathbf{r}|^2}, \quad (3.5)$$

$$\psi_{2p_x}(\mathbf{r}) \approx \sum_i c_i (x - \beta_i) e^{-\alpha_i |\mathbf{r}|^2}. \quad (3.6)$$

In this case c_i are the contraction coefficients and α_i are the exponents of the Gaussian functions and β_i are optional parameters adjusted to improve the fit.

In the next step, Wannier functions are constructed, as described in the flowchart in Fig. 3.1, involving the orthogonalization and normalization of the trial basis set. Typically used in solid-state physics, Wannier functions are wavefunctions that are centered at a particular region in a system, usually around an atomic site or a specific location in a crystal lattice. Unlike Bloch functions, which are delocalized and extend over the entire crystal due to their periodic nature, Wannier functions decay rapidly and have significant values only within a limited region of space.

One might ask how to define molecular Wannier functions, which are calculated as the lattice Fourier transform of Bloch functions. We postulate the molecular Wannier function as a function in the form of a linear combination of neighboring atomic orbitals in the form

$$w_i(\mathbf{r}) = \beta (\phi_i(\mathbf{r}) - \gamma \phi_{i+1}(\mathbf{r})), \quad (3.7)$$

where ϕ_i is an atomic orbital, ϕ_{i+1} denotes the neighboring atomic orbital, and β and γ are the so-called mixing parameters. In this sense, the functions provide a natural extension of the concept of atomic orbitals.

We select Wannier functions that are inherently localized in space. Constructing them as linear combinations of localized atomic orbitals aligns with this property. The coefficients β and γ should be chosen to ensure the orthogonality and normalization of the such functions. In many molecules, especially those with covalent bonding, atomic orbitals on neighboring sites overlap and hybridize.

The concept of locality is deeply rooted in many concepts of quantum chemistry such as Atoms in Molecules, Natural Bond Orbitals, Valence Bond theory. However, it also

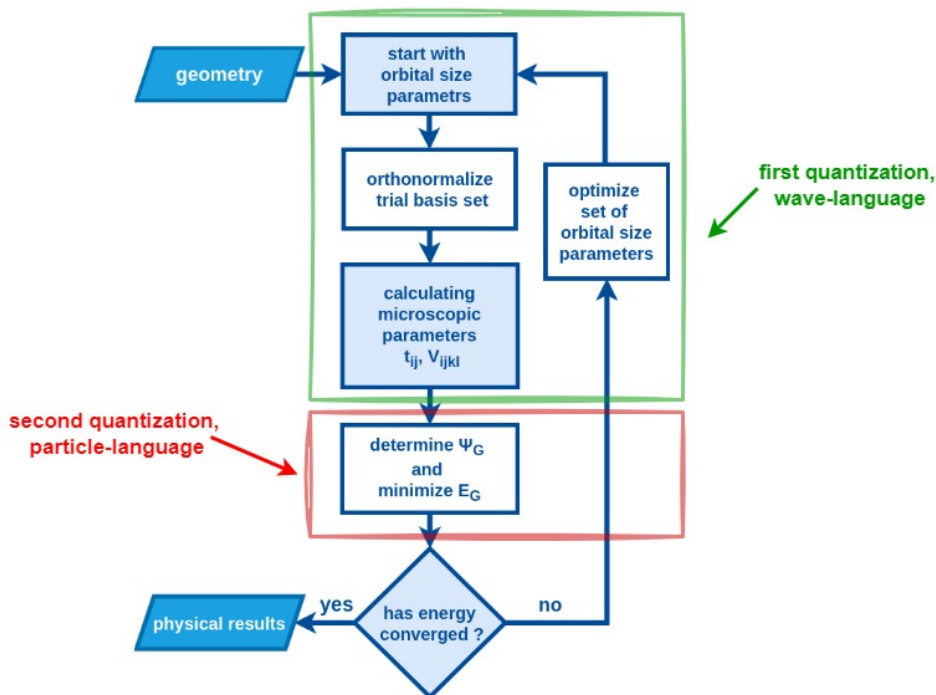


Figure 3.1: Flowchart of the EDABI method. The process begins with the selection of a trial single-particle basis of wave functions (6), followed by the diagonalization of the many-particle Hamiltonian. By optimizing the single-particle state size, the method explicitly determines the parameters of the trial wave function, microscopic interaction and hopping parameters, ground-state energy, and the explicit form of the many-particle wave function, all within the correlated interacting state for a given interatomic distance. The step highlighted in green indicates the stage based on the first quantization, whereas the step highlighted in red pertains to the diagonalization of the Hamiltonian in the second quantization.

aligns with chemical intuition developed from the knowledge created when chemistry was solely an experimental branch of science. There are several theories where locality is at variance with them. As an example, one can mention Density Functional Theory (DFT), Coupled Cluster (CC), and finally Molecular Orbitals theory (MO). In such cases, the orbitals can be completely delocalized over the whole molecule.

Summarizing briefly, our approach combines the first and second quantization methods. In the first quantization, it uses the concept of Wannier functions, effectively merging local theories (like Valence Bond Theory) with non-local ones (such as Molecular Orbital Theory, exemplified by the two-particle wave function obtained through Hamiltonian diagonalization). Also as a supplement, in Fig. 3.2 we list most popular wave-functions used historically to describe a single bond. This comparison of our approach with other methods, both historical and current, was the subject of a chapter published in *Advances in Quantum Chemistry* [?].

As our method involved not only first quantization language, constructing the basis composed from atomic or Wannier orbitals is insufficient. It serves as a basis to define the field operators and effectively to obtain the total Hamiltonian in the second quantization representation (in the Fock space).

In this situation, the field operators are in the form

Two-particle wave functions			
Ansatz	Hartree-Fock I	$A[\varphi_A(\mathbf{r}_1)\chi_{\uparrow}(1)\varphi_B(\mathbf{r}_2)\chi_{\downarrow}(2) - \varphi_A(\mathbf{r}_2)\chi_{\uparrow}(2)\varphi_B(\mathbf{r}_1)\chi_{\downarrow}(1)]$ $\equiv \varphi_A(\mathbf{r}_1)\varphi_B(\mathbf{r}_2)[\chi_{\uparrow}(1)\chi_{\downarrow}(2) - \chi_{\downarrow}(1)\chi_{\uparrow}(2)]$	antysymmetrized spinorbitals
	Heitler-London (1927)	$[\varphi_A(\mathbf{r}_1)\varphi_B(\mathbf{r}_2) \pm \varphi_A(\mathbf{r}_2)\varphi_B(\mathbf{r}_1)]$	covalent part
	Spin Coupled Valence Bond (Hartree-Fock II)	$A[\varphi_A(\mathbf{r}_1)\varphi_B(\mathbf{r}_2) \pm \varphi_A(\mathbf{r}_2)\varphi_B(\mathbf{r}_1)]$ $+ (1 - A)[\varphi_A(\mathbf{r}_1)\varphi_A(\mathbf{r}_2) \pm \varphi_B(\mathbf{r}_2)\varphi_B(\mathbf{r}_1)]$ $\times [\chi_{\uparrow}(1)\chi_{\downarrow}(2) \mp \chi_{\downarrow}(1)\chi_{\uparrow}(2)]$	covalent part ionic part spin-part
	Coulson-Fisher (1949)	$A[\Phi_A(\mathbf{r}_1)\Phi_B(\mathbf{r}_2) \pm \Phi_A(\mathbf{r}_2)\Phi_B(\mathbf{r}_1)]$	covalent part
Configurational Interaction		$\sum_{\{i\}} c_i \det(\varphi_i(\mathbf{r}))$	multiple Slater determinants
Exact Diagonalization Ab Initio		$C[w_A(\mathbf{r}_1)w_B(\mathbf{r}_2) \pm w_A(\mathbf{r}_2)w_B(\mathbf{r}_1)]$ $+ I[w_A(\mathbf{r}_1)w_A(\mathbf{r}_2) \pm w_B(\mathbf{r}_2)w_B(\mathbf{r}_1)]$ $\times [\chi_{\uparrow}(1)\chi_{\downarrow}(2) \mp \chi_{\downarrow}(1)\chi_{\uparrow}(2)]$	covalent part ionic part spin-part

$\varphi_i(\mathbf{r})$ - atomic wave function

$$\Phi_i(\mathbf{r}) = \varphi_i(\mathbf{r}) + \lambda\varphi_{i+1}(\mathbf{r})$$

$$w_i(\mathbf{r}) = \beta[\varphi_i(\mathbf{r}) + \gamma\varphi_{i+1}(\mathbf{r})]$$

- two equivalent variants of molecular orbitals (MO)

Figure 3.2: The development of the two-particle wave function form progresses from the original Hartree-Fock method (Hartree-Fock I), through the Heitler-London approach (initially excluding the spin component), followed by the spin-coupled valence bond model introduced by Coulson and Fisher, and finally to the Configuration Interaction method (which involves a linear combination of Slater determinants for various electron occupancies). The final expression represents the result obtained using our EDABI method.

$$\hat{\psi}^\dagger(\mathbf{r}) \equiv \sum_i w_i^*(\mathbf{r}) \hat{a}_i^\dagger, \quad (3.8)$$

$$\hat{\psi}(\mathbf{r}) \equiv \sum_i w_i(\mathbf{r}) \hat{a}_i, \quad (3.9)$$

where $w_i(\mathbf{r})$ denotes Wannier function. Details regarding the derivation of the Hamiltonian based on field operators can be found in [32]. One can notice that possible is the inverse operation, where the two-particle wave function is calculated from the second quantized wave function and field operator [33, 2].

3.2 All-interaction molecular Hamiltonian

The starting point for our model is the complete non-relativistic Hamiltonian that describes all interactions for diatomic molecular systems, which can be expressed in the language of second quantization as follows

$$\begin{aligned} \hat{\mathcal{H}} = & \epsilon_a \sum_{i\sigma} \hat{n}_{i\sigma} + \sum'_{ij\sigma} t_{ij} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \frac{1}{2} \sum'_{ij\sigma\sigma'} K_{ij} \hat{n}_{i\sigma} \hat{n}_{j\sigma'} \\ & - \frac{1}{2} \sum'_{ij} J_{ij}^H \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j - \frac{1}{4} \hat{n}_i \hat{n}_j \right) + \frac{1}{2} \sum'_{ij} J'_{ij} (\hat{a}_{i\uparrow}^\dagger \hat{a}_{i\downarrow}^\dagger \hat{a}_{j\downarrow} \hat{a}_{j\uparrow} + \text{H.c.}) \\ & + \frac{1}{2} \sum'_{ij\sigma} V_{ij} (\hat{n}_{i\sigma} + \hat{n}_{j\sigma}) (\hat{a}_{i\bar{\sigma}}^\dagger \hat{a}_{j\bar{\sigma}} + \text{H.c.}) + \mathcal{H}_{\text{ion-ion}}, \end{aligned} \quad (3.10)$$

where Hermitian conjugation is indicated by $H.c.$. Fermionic annihilation and creation operators for a particular state labeled as i and a given spin σ are denoted as $\hat{a}_{i\sigma}$ and $\hat{a}_{i\sigma}^\dagger$, respectively. The number operator for spin σ at site i , represented as $\hat{n}_{i\sigma}$, is defined by the expression $\hat{a}_{i\sigma}^\dagger \hat{a}_{i\sigma}$. Additionally, the overall number operator for site i , $\hat{n}_i$, aggregates the counts from both spin-up and spin-down states, expressed as $\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}$. Spin dynamics at each site are encapsulated by the operator $\hat{\mathbf{S}}_i$, which equals $\frac{1}{2} \sum \alpha\beta \hat{a}_{i\alpha}^\dagger \boldsymbol{\sigma}^{\alpha\beta} \hat{a}_{i\beta}$, where $\boldsymbol{\sigma}_i^{\alpha\beta}$ symbolizes the Pauli matrices. The Hamiltonian under consideration comprises several components: atomic and hopping contributions scaled by ϵ_a and t_{ij} respectively, the Hubbard interaction characterized by U that reflects the intra-atomic interactions between particles on the same atomic site with opposite spins, and direct intersite Coulomb interactions denoted by K_{ij} . It also includes Heisenberg exchange interactions given by J_{ij}^H , alongside terms for two-particle and correlated hopping and intersite Coulomb interactions scaled by J'_{ij} and V_{ij} . The ion-ion Coulomb interaction, considered here in its classical representation, completes the Hamiltonian. The detailed computation of these microscopic parameters (ϵ_a , t_{12} represented as t , U , $K_{12} = K$, $J_{12}^H = J'_{12}$, and $V_{12} = V$) is rigorously adjusted based on the single-particle wave function dimensions. Summations denoted by primes are restricted to terms where $i \neq j$.

An unquestionable advantage of the formalism of second quantization is the intuitive description of the physical system in the language of particles. Fig. 3.3 illustrates various interaction terms in a two-atom molecule which interactions are fundamental to understanding its electronic structure and behavior of the molecule. Here is a concise description of each interaction shown in the figure.

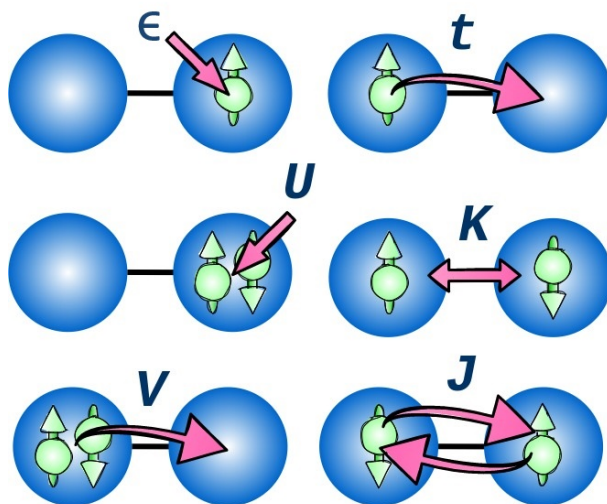


Figure 3.3: The illustration of various interaction processes in molecular systems. It includes several key components: a single-particle excitation process, the hopping of an electron between neighboring sites, the on-site Coulomb repulsion between electrons, the direct exchange interaction between sites, the inter-site Coulomb interaction, and the indirect exchange interaction, also known as superexchange. V is the so-called correlated hopping term. The green arrows indicate the particle with spin, while the pink arrows illustrate the interaction pathways.

An atomic orbital energy is presented as single electron on one atomic side and indicated by straight purple arrow.

An electron hopping is marked as curved purple arrow indicating movement of electron from one atom to a neighboring atom. This process represents the kinetic energy associated with the movement of electrons between atomic sites and accounts for the delocalization of electrons across the molecule.

Hubbard interaction, which occurs when two electrons occupy the same atomic orbital on a single atom. The figure shows two electrons on the same atom with their spins paired, indicating Coulomb repulsion. The on-site Coulomb repulsion term U describes the energy cost due to this electron-electron repulsion, which discourages double occupancy of the same orbital.

The figure depicts electrons on neighboring atoms interacting via Coulomb repulsion. The inter-site Coulomb interaction term K accounts for the repulsive interaction between electrons located on different atoms. This term is crucial for understanding how electrons on different sites influence each other, contributing to the overall electrostatic energy of the molecule.

Fig. 3.3 illustrates the exchange of spins between neighboring atoms. This interaction, described by the spin-exchange term J , represents the quantum mechanical process where the spins of electrons on adjacent atoms interact. The Heisenberg spin-exchange interaction is significant for magnetic properties and spin correlation effects in the molecule.

It shows pair hopping and pairing interactions. The pair hopping term V describes the process where electron pairs hop between different sites, while the pairing term J involves interactions that can lead to the formation of electron pairs. These interactions are essential for phenomena such as superconductivity and pairing mechanisms in correlated electron systems.

The numerical implementation of the EDABI method has been the subject of several studies, and it has been implemented here [34] for the first time in C++ for molecular systems and nanosystems. In the work Ref. [4], the method has been extended and numerically optimized.

3.3 Ground state energy and orbital size contraction

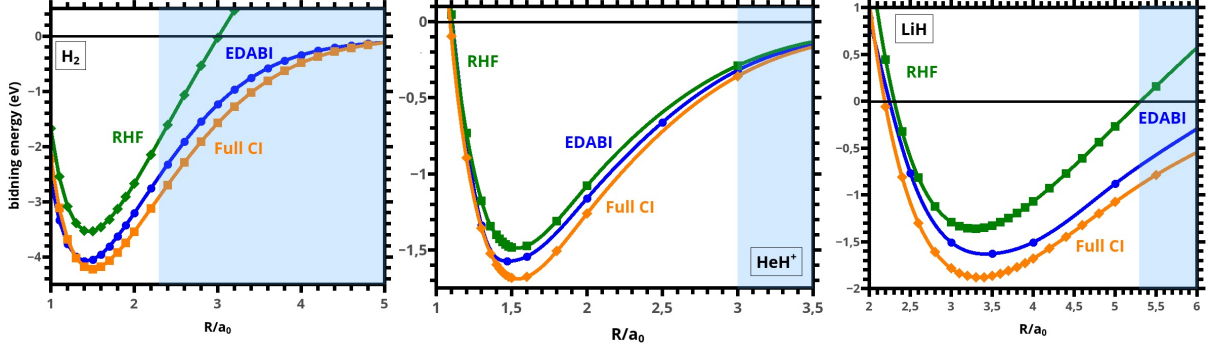


Figure 3.4: The H_2 , HeH^+ , and LiH binding energy versus relative interatomic distance, obtained using EDABI method and compared with restricted Hartree-Fock (RHF) and full configuration interaction (full CI) approach. a_0 is the Bohr radius.

In Fig. 3.4, we present the binding energy of H_2 , HeH^+ , and LiH , respectively, comparing our EDABI method results with those obtained from configuration interaction (CI) and restricted Hartree-Fock (RHF) calculations using the 6-31G* basis set. The EDABI results are specifically for the $1s$ state. Notably, for small interatomic distances $R < R_{\text{bond}}$ (at the minimum), the EDABI method yields slightly lower energies compared to full CI. This lower energy in the EDABI method for the $1s$ states is most likely due to the renormalization of the orbital sizes. This slight discrepancy should not significantly affect the subsequent discussion focused on the large- R limit, which is our primary concern here. It is worth mentioning that both CI and EDABI are variational approaches, and the optimization of the wave-function size at small R might be as crucial as including higher excited states. The binding energy is defined as $E_{\text{bind}} = E - 2E_H$ (where E is the energy obtained from the respective method and E_H denotes energy of an isolated atom).

3.4 The exact solution of the Heitler-London model

For a two-site system, like a hydrogen molecule, a comprehensive analysis of the electronic state can be performed starting from the all-interactions Hamiltonian, like that from Eq. (3.10). The trial basis can be constructed in the second quantization language in the following manner. Because hydrogen molecule is consistent from two electrons and two nuclei there are six possible electronic states, three triplet states

$$\begin{cases} |1\rangle = \hat{a}_{1\uparrow}^\dagger \hat{a}_{2\uparrow}^\dagger |0\rangle, \\ |2\rangle = \hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger |0\rangle, \\ |3\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle, \end{cases} \quad (3.11)$$

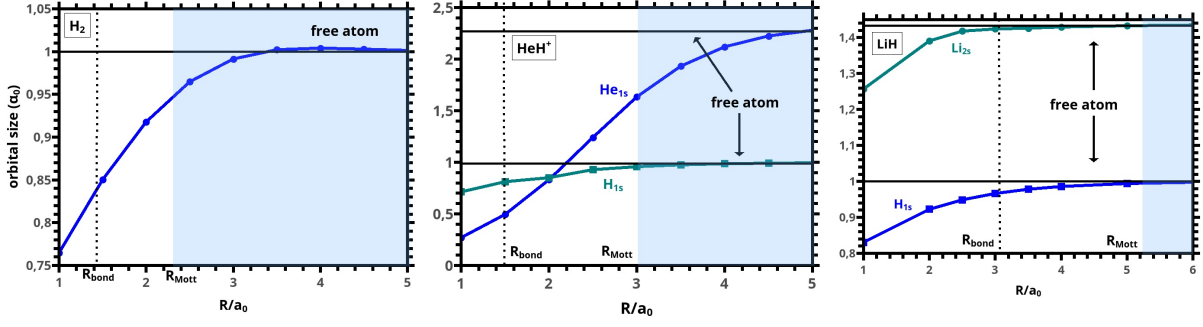


Figure 3.5: Illustration of the renormalization of orbital sizes (in atomic units) as a function of the interatomic distance R for different molecules: H_2 , HeH^+ , and LiH . The left panel shows H_2 with H_2 and H orbital sizes, the middle panel shows HeH^+ with He and H orbital sizes, and the right panel shows LiH with Li and H orbital sizes. The shaded regions indicate the transition from molecule-bound states to free atomic states.

and three singlet states

$$\begin{cases} |4\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger - \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle, \\ |5\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger + \hat{a}_{2\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle, \\ |6\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger - \hat{a}_{2\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle. \end{cases} \quad (3.12)$$

In accordance with the Hamiltonian, the eigenvalues for triplet states are degenerated and can be written as

$$E_1 = E_2 = E_3 = 2\varepsilon + K - J. \quad (3.13)$$

For the singlet states, the Hamiltonian submatrix is

$$\mathcal{H}_{ij} = \begin{pmatrix} 2\varepsilon + K + J & 2(t + V) & 0 \\ 2(t + V) & 2\varepsilon + K + U & U \\ 0 & U & 2\varepsilon + U - J \end{pmatrix}. \quad (3.14)$$

which diagonalized gives three different eigenvalues

$$E_{4,5} = 2\varepsilon + \frac{K + U}{2} + J \pm \sqrt{(U - K)^2 + 16(t + V)^2}, \quad (3.15)$$

and

$$E_6 = 2\varepsilon + U - J. \quad (3.16)$$

All eigenvalues are plotted as functions of interatomic distance in Fig. 3.6. The HOMO-LUMO (highest occupied molecular orbitals and lowest unoccupied molecular orbital) gap, which is on the $U - K$ energy scale is also depicted. The blue area

For the case where correlation energy dominates, i.e. $(U - K) \gg 4|t + V|$, singlet eigenvalues take form

$$E_4 \approx \varepsilon_1 + \varepsilon_2 + (U + K + J) + \frac{4(t - V)^2}{U - K}, \quad (3.17)$$

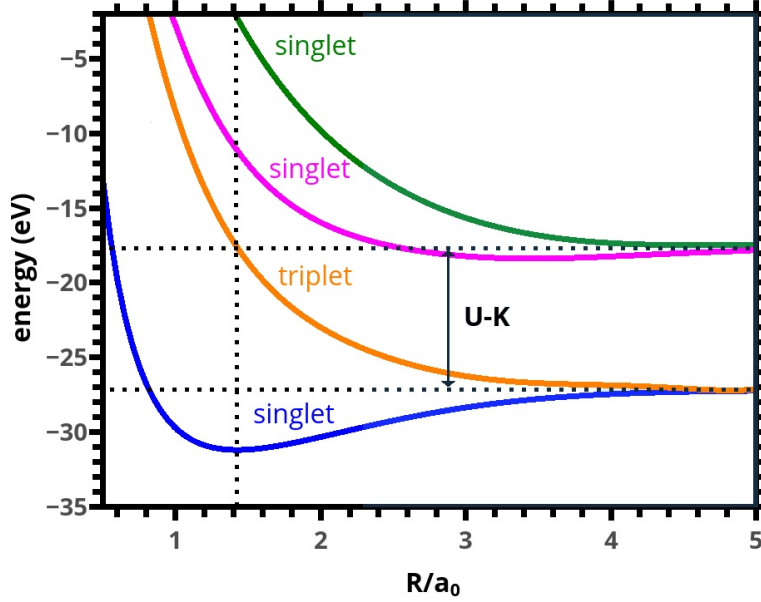


Figure 3.6: The lowest energy levels include three singlets and three triplet states as functions of interatomic distance R . The scale $U - K$ denotes the effective repulsive Coulomb interaction between electrons, representing the HOMO-LUMO gap. As the interatomic distance R increases, the states exhibit a more pronounced atomic character.

$$E_5 \approx \varepsilon_1 + \varepsilon_2 + J - \frac{4(t - V)^2}{U - K}. \quad (3.18)$$

Assuming $J > 0$ (implying the ferromagnetic character of direct spin exchange interaction), the condition for the stability of the triplet ground state is

$$\frac{4(t - V)^2}{U - K} < J, \quad (3.19)$$

with the singlet as the ground state in the opposite case. The comparison of these two spin-exchange interactions is discussed in [35].

The corresponding singlet ground state in the Fock space takes the form

$$|\Psi_G(\mathbf{r}_1, \mathbf{r}_2)\rangle = \frac{2(t + V)}{\sqrt{2D(D - U + K)}} (\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger - \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle \quad (3.20)$$

$$- \frac{1}{2} \sqrt{\frac{D - U + K}{2D}} (\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle. + \quad (3.21)$$

Using this result, and the definition of wave-function calculating using the field-operator representation

$$\Psi_G(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \langle 0 | \hat{\psi}(\mathbf{r}_1) \hat{\psi}(\mathbf{r}_2) | \Psi_G(\mathbf{r}_1, \mathbf{r}_2) \rangle, \quad (3.22)$$

and the relation from Eq. (3.9) we can write the ground-state two-particle exact wave function as

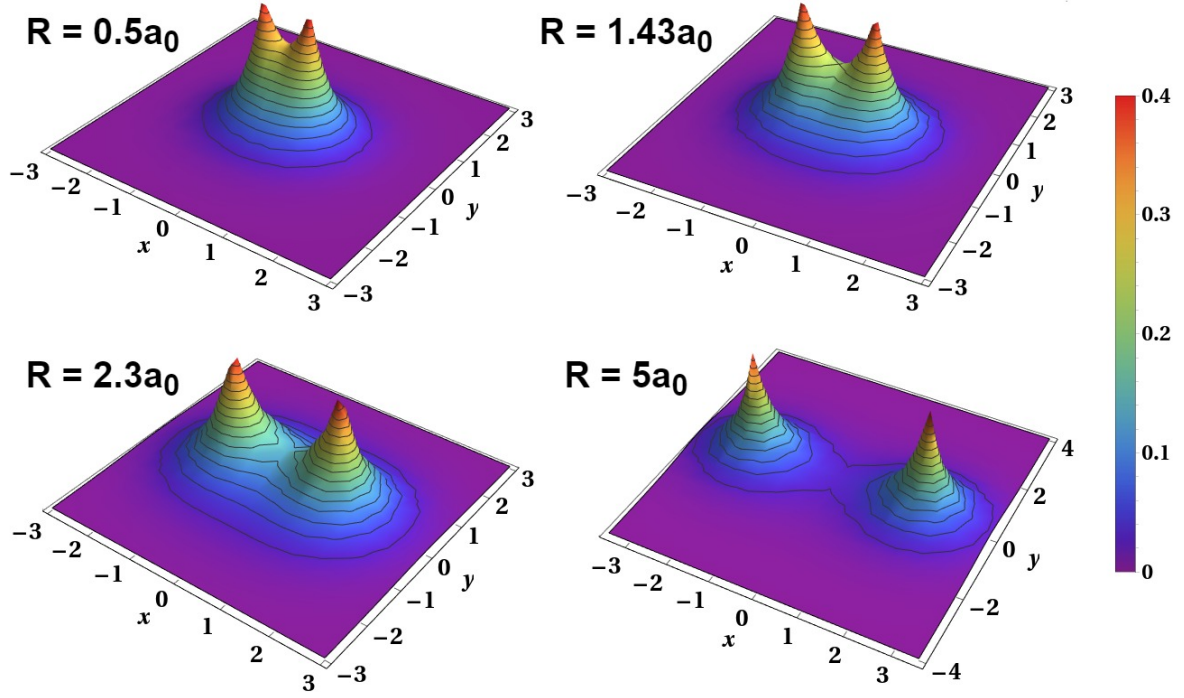


Figure 3.7: Electron density $n_\sigma(\mathbf{r})$ shown for different interatomic distance (a) $R = 1a_0$, (b) $R = 1.43a_0$, (c) $R = 2.3a_0$, (d) $R = 4a_0$. the regions centred at the nuclei become nearly disjoint, highlighting the persistence of atomic behavior at these distances. This

$$\begin{aligned} \Psi_G(\mathbf{r}_1, \mathbf{r}_2) = & \frac{2(t+V)}{\sqrt{2D(D-U+K)}} [w_1(\mathbf{r}_1)w_2(\mathbf{r}_2) + w_1(\mathbf{r}_2)w_2(\mathbf{r}_1)] [\chi_\uparrow(\mathbf{r}_1)\chi_\downarrow(\mathbf{r}_2) - \chi_\downarrow(\mathbf{r}_1)\chi_\uparrow(\mathbf{r}_2)] \\ & - \frac{1}{2} \sqrt{\frac{D-U+K}{2D}} [w_1(\mathbf{r}_1)w_1(\mathbf{r}_2) + w_2(\mathbf{r}_1)w_2(\mathbf{r}_2)] [\chi_\uparrow(\mathbf{r}_1)\chi_\downarrow(\mathbf{r}_2) - \chi_\downarrow(\mathbf{r}_1)\chi_\uparrow(\mathbf{r}_2)] \end{aligned} \quad (3.23)$$

We transform from the first quantization language to the second quantization to allow us a more intuitive physical interpretation of chemical bonds in terms of particle densities. Specifically, we focus on the electron density as calculated by the field operator, providing insight into the nature of the bond. The electron density for a spin state σ is given by

$$n_\sigma(\mathbf{r}) = \langle \psi_G | \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) | \psi_G \rangle, \quad (3.24)$$

where $|\psi_G\rangle$ is the ground-state wave function, and $\hat{\psi}_\sigma(\mathbf{r})$ is the field operator for electrons with spin σ . This density, when summed over both spin states ($\sigma = \uparrow, \downarrow$), yields the total electron density:

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}) = 2n_\sigma(\mathbf{r}). \quad (3.25)$$

Here, we have spin symmetry, so $n_\uparrow(\mathbf{r}) = n_\downarrow(\mathbf{r})$. To illustrate the behavior of electron density, we present in Fig. 3.7 several panels showing $n(\mathbf{r})$ in the (x, y) plane for different interatomic distances: $R/a_0 = 1, 1.43$ (the bond distance, R_{bond}), 2.3 (the Mott transition distance, R_{Mott}), and 4 . These panels reveal how the electron density evolves with increasing separation between the protons.

The electron density $n(\mathbf{r})$ offers a more physically intuitive measure than the probability density $|\psi_G(\mathbf{r}_1, \mathbf{r}_2)|^2$. In particular, $n(\mathbf{r})$ highlights the spatial distribution of electrons and how it changes as the atomic separation increases. As R surpasses R_{Mott} , the electron density between the atoms decreases rapidly, indicating the transition to a regime where atomic characteristics dominate.

To quantify this transition, we examine the electron density at the midpoint between the protons, $n(0, 0)$. Table 3.1 lists $n(0, 0)$ for various interatomic distances, along with the inverse orbital size and mixing coefficients of the wave function $w_i(\mathbf{r}) = w(\mathbf{r} - \mathbf{R}_i)$. These values confirm that single-particle and two-particle characteristics evolve towards their atomic limits as R increases beyond R_{Mott} .

Table 3.1: Particle density at the midpoint, inverse orbital size α_0 , and mixing coefficients β and γ , all versus R . The particle density $n(0, 0)$ illustrates the gradually vanishing electron density in the region between the atoms as R increases beyond R_{Mott} .

$R (a_0)$	$n(0, 0)$	α_0	β	γ
1	0.334	1.30751	1.1386	0.47811
1.43	0.267	1.19838	1.0854	0.38877
2.3	0.142	1.05428	1.0338	0.25358
4	0.023	0.998601	1.0012	0.048640

The decrease in the mixing coefficient γ reflects the reduction in Pauling covalency, while $n(0, 0)$ directly measures the true covalency of the bond. This analysis underscores the utility of second quantization in providing a clear, physical picture of electron density and bonding behavior.

Chapter 4

Fundamental quantum features of the bonding

Applying a combined approach of first and second quantization allows for the description and characterization of various fundamental features of molecular systems, which are unattainable using methods considered state-of-the-art in quantum chemistry. Given that the hydrogen molecule is a standard example in quantum chemistry and molecular physics, and since our calculations for the hydrogen molecule can be carried out rigorously in a mathematical sense, we have restricted our description of new fundamental features of molecular systems mostly on this canonical example.

4.1 Mott-Hubbard criterion and correspondence to infinite systems

The general concept of the Mott-Hubbard effect originates from condensed matter physics and describes the phenomenon where materials that are expected to be conductive (metals) based on band theory, become insulators due to strong electronic interactions [36, 37]. The criterion can be expressed as $U \simeq W$, where $W \equiv |\sum_{j(i)} t_{ij}|$ is the bare bandwidth. The transition often takes the form of a discontinuous metal-insulator transition for an odd integer number of relevant valence electrons per atom.

Translating this concept of the Mott-Hubbard localization-delocalization to the realm of molecular physics demands a new description and interpretation of this phenomenon. In molecular systems, such as H_2 , HeH^+ , and LiH , the HOMO-LUMO splitting must exceed the effective interatomic hopping amplitude $W = 4|t|$. For extended Hamiltonian (3.10), the Mott-Hubbard criterion takes then the form $r \equiv (U - K)/(2|t + V|)$ so that both the correlated hopping and intersite Coulomb interaction contribute, in addition to t and U .

In this context, the criterion distinguishes qualitatively between the regime of strong correlations ($r \geq 1$) and that of moderate to weak correlations ($r < 1$) [35].

The calculations related to the Mott-Hubbard criterion were part of the research published in our first paper [35], where we investigated not only the characteristic interatomic distance separating these two regimes for three selected molecular systems. We also examined which types of interactions are important for calculating this criterion in molecular systems, leading us to conclude that it is necessary to consider the interactions t , U , K , and V .

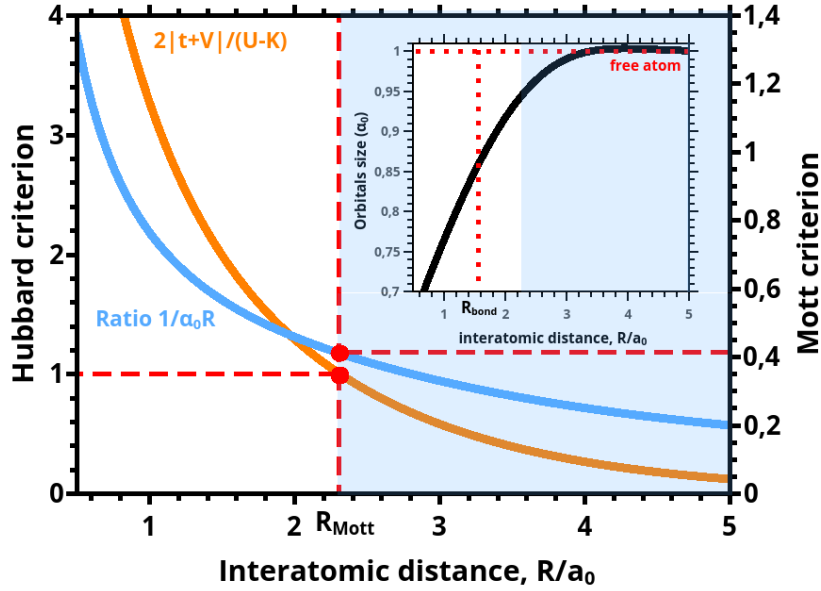


Figure 4.1: The plot showcases the behavior of atomicity as a function of interatomic distance R for both Hubbard (orange) and Mott (blue) criteria. Dashed horizontal lines represent these characteristics. Dots indicate specific points that meet the Hubbard and Mott conditions. A vertical dotted line highlights the beginning of Mott-Hubbard regime at R_{Mott} .

Fig. 4.1 demonstrates the transition from a molecular H_2 state, where electrons are paired, to individual, separate atomic states with singly occupied orbitals. This transition is analogous to Mott-Hubbard localization, where a system shifts from a conductive to an insulating state due to strong electronic interactions. The diagram highlights the criteria for Mott and Hubbard onsets, showing the critical points where localized (atomic) behavior emerges. The evolution depicted aligns with the principles discussed in the context of atomicity, where atomicity and true covalency intersect at the Mott-Hubbard localization interatomic distance, as detailed in the next Chapter.

Table 4.1: The interatomic distance corresponding to the Mott boundary regime and bond length calculated for H_2 , HeH^+ , and LiH molecules within the use of EDABI method.

System	Mott boundary (a_0)	Bond length (a_0)
H_2	2.3	1.43
HeH^+	3.0	1.47
LiH	5.3	3.38

Table 4.1 presents the Mott-Hubbard critical distance R_{Mott} . Comparison with the bond length R_{bond} indicates that crossing the Mott-type boundary is only possible when the molecules are further apart, which can be artificially achieved by placing them on surfaces with an external force elongating them. A particularly favorable situation arises when molecules are placed in an environment with a high dielectric constant, as this weakens the interaction and increases the bond length. Therefore, the entire analysis must be reconsidered to include a realistic configuration with the appropriate external (surface) potential.

4.2 The concept of the true covalency and atomicity

As highlighted in the introduction, since the inception of theoretical chemistry, and quantum chemistry, in particular, researchers have been attempting to numerically define the characteristics of chemical bonding, specifically its ionicity and covalency. Nonetheless, many of these definitions are dependent on the method used, where both covalency and ionicity hinge on the chosen computational approach. Moreover, there remains the issue identified in the introduction, related to the unphysical behavior of covalency at the dissociation limit.

Such behavior led us to conclude that a bonding characteristic based solely on the concepts of covalency and ionicity is incomplete. Since a molecule arises from two atoms, the atomic character of the constituent atoms must be present all the time. The heuristic definition of ionicity is as follows: an ionic bond is one in which at least one electron transfers from its parent atom to a neighboring atom. A covalent bond, on the other hand, is characterized by atoms sharing their electrons. This can be schematically represented as shown in Fig. 4.2.

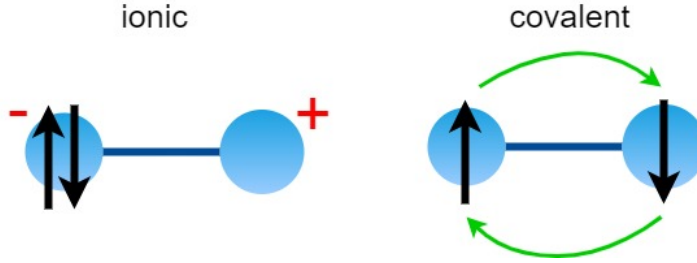


Figure 4.2: Pictorial representation of the heuristic definition of ionic and covalent bonding

A simple analysis of interactions, supported by an illustration of these interactions in Fig. 3.3, may lead to the conclusion that the U Hubbard interaction promotes covalent bonding, and the hopping integral is responsible for the covalent type of bonding. Although this statement is not far from the truth, it is not fully sufficient to describe a system that, though consisting of two fermions, is nonetheless complex. Our method allows for the examination of how microscopic parameters and dynamic contributions depend on interatomic distances, which are the subject of Chapter 4, describing entangled correlations using the molecule H_2 as an example.

At this point, one can use the exact wave function from Chapter 2 to define mathematical ionicity and covalency, which was provided by Heitler and London and Mulliken, and which directly originates from the aforementioned. The two-particle exact wave function can be written in the following form

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \underbrace{\frac{2(t+V)}{\sqrt{2D(D-U+K)}}}_{\text{covalent factor}} \underbrace{\Psi_c(\mathbf{r}_1, \mathbf{r}_2)}_{\text{covalent part}} - \underbrace{\frac{1}{2} \sqrt{\frac{D-U+K}{2D}}}_{\text{ionic factor}} \underbrace{\Psi_i(\mathbf{r}_1, \mathbf{r}_2)}_{\text{ionic part}}, \quad (4.1)$$

where t , U , V , and K are proper microscopic parameters which were previously defined. Covalent and ionic wave functions composed of Wannier functions are labelled as $\Psi_c(\mathbf{r}_1, \mathbf{r}_2)$ and $\Psi_i(\mathbf{r}_1, \mathbf{r}_2)$, respectively. By denoting the covalent and ionic coefficients of the wave function as C and I , respectively, we can define the covalent and ionic contributions to the total wave function as follows

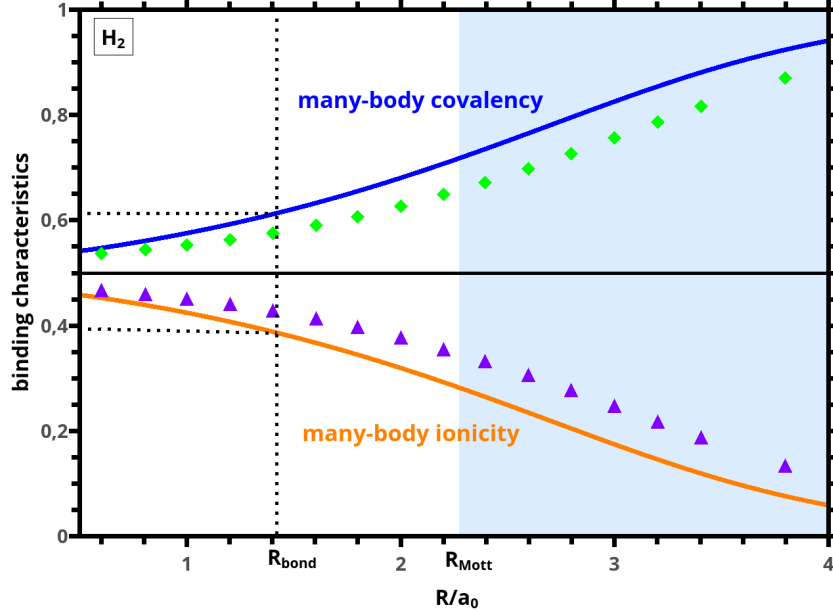


Figure 4.3: Comparison of the ionicity and covalency for hydrogen molecule calculated in our method and Decoding real space bonding descriptor and repeated after [24] following the method decoding real space bonding descriptors.

$$\text{covalency: } \gamma_c = \frac{C^2}{C^2 + I^2} = \frac{16(t + V)^2}{16(t + V)^2 + (D - U + K)^2} \quad (4.2)$$

$$\text{ionicity: } \gamma_i = \frac{I^2}{C^2 + I^2} = \frac{(D - U + K)^2}{16(t + V)^2 + (D - U + K)^2} \quad (4.3)$$

In our case, covalency and ionicity are not merely numerical outcomes derived from the optimization of the wave function. They represent the contributions of individual interactions to the total energy. The analysis of these interactions is typical in examining the characteristics of bonding. What is novel here is that the total energy is not composed within the framework of a single numerical method; instead, the contributions are explicitly calculated within a variational method made possible by integrating the languages of first and second quantization.

This result led us to the relationship plotted in the graph in Fig. 4.3, where covalency and ionicity are shown as functions of interatomic distance and compared with the result obtained using real space bonding descriptors in valence bond language. It is clear that such behavior of covalency, in terms of chemical bonding, is unphysical as it takes maximal value (unity) in the limit of separated atoms limit.

As mentioned earlier, the characterization of bonding based solely on the wave function is incomplete and must be supplemented with the atomic contribution to the nature of the bond. To capture this, it was necessary to transform the function form Eq. (4.1) into a form based on atomic wave functions.

$$\begin{aligned} \Psi_0(\mathbf{r}_1, \mathbf{r}_2) &= \left(C\beta^2(1 + \gamma^2) - 2\gamma I\beta^2 \right) \phi_{cov}^{at}(\mathbf{r}_1, \mathbf{r}_2) + \left(I\beta^2(1 - \gamma^2) - 2\gamma C\beta^2 \right) \phi_{ion}^{at}(\mathbf{r}_1, \mathbf{r}_2) \\ &\equiv \tilde{C}\phi_{cov}^{at} + \tilde{I}\phi_{ion}^{at}, \end{aligned} \quad (4.4)$$

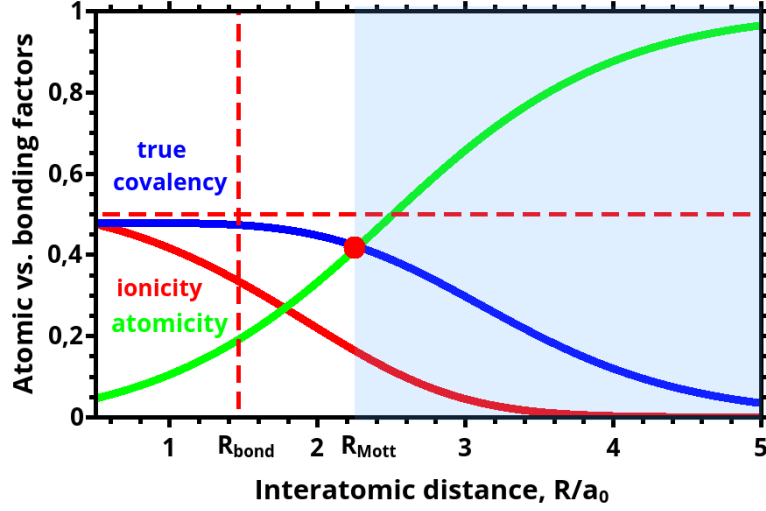


Figure 4.4: Intrinsic characteristics of chemical bond: atomicity (green), true covalency (blue), and ionicity (red) as functions of R . In the limit $R \rightarrow 0$, atomicity essentially vanishes, while it becomes the dominant contribution in the separate-atom limit as $R \rightarrow \infty$. The solid circle marks the onset of localization effects, or *Mottness*, arising from interelectronic correlations. Blue shaded area means Mott-Hubbard regime.

where the coefficients now depend not only on microscopic parameters but also on the mixing coefficients β and γ , defined in Eq. 3.7.

Now, we need to ask how to define the atomic contribution. By analyzing the behavior of covalency from Eq. (4.2) and the form of the new wave function (Eq. (4.4)), we can conclude that the part of this function that remains nonzero (and even increases) in the limit where atomic functions do not mix, i.e., $\gamma \rightarrow 0$, provides the atomic contribution to the wave function. Therefore, we need to calculate the limit for the coefficient C , which can be expressed as

$$\lim_{\gamma \rightarrow 0} \tilde{C} = C\beta^2 \equiv \tilde{A}, \quad (4.5)$$

which we adopt as a definition of atomic coefficient $\tilde{A}$. Now, one can postulate new definitions of true covalency, ionicity, and atomicity as [38]

$$\text{true covalency: } \gamma_{cov} \equiv \frac{|\tilde{C}|^2 - |\tilde{A}|^2}{|\tilde{C}|^2 + |\tilde{I}|^2}, \quad (4.6)$$

$$\text{ionicity: } \gamma_{ion} \equiv \frac{|\tilde{I}|^2}{|\tilde{C}|^2 + |\tilde{I}|^2}, \quad (4.7)$$

$$\text{atomicity: } \gamma_{at} \equiv \frac{|\tilde{A}|^2}{|\tilde{C}|^2 + |\tilde{I}|^2}. \quad (4.8)$$

Those quantities compose the fundament of the subsequent physical discussion in the remaining part of the thesis.

4.3 Dynamic contributions to ground state energy

There are several methods in molecular physics and quantum chemistry which are based on the analysis of the contribution of proper energy components to the total energy. In our approach, because we have the exact solution of the Heitler-London of the hydrogen molecule, we can calculate mathematically exactly the averages of the operator parts of the Hamiltonian (dynamic contributions) of the different terms, contributing to the total energy. This method aligns with the principles of dynamic contributions, as it provides a detailed and rigorous way to understand electronic behavior and interactions within a molecular or solid-state system. There is also one advantage of our approach in the context of chemical bonding investigation. We can calculate dynamic contribution as a function of covalent C and ionic I factor.

Orbital energy dynamic contribution is the term that represents the energy associated with electrons occupying the atomic orbitals. It is a measure of the intrinsic energy levels of the orbitals involved in bonding. For a hydrogen molecule, this is typically a constant value and does not depend on the interaction strengths, as it is a measure of the baseline energy associated with occupying these orbitals.

$$\langle \hat{D}_\epsilon \rangle = \langle \Psi_G | \hat{a}_{i\sigma}^\dagger \hat{a}_{i\sigma} | \Psi_G \rangle = 1. \quad (4.9)$$

Hopping describes the kinetic energy contribution due to the hopping of electrons between different sites (atoms). In the context of a hydrogen molecule, it is directly related to the hopping integral t , which measures the probability amplitude for an electron to move from one site to another multiplied by the average value of the operator in the following form

$$\langle \hat{D}_t \rangle = \langle \Psi_G | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} | \Psi_G \rangle = 16|CI| \quad (4.10)$$

On-site Coulomb interaction accounts for the repulsive interaction between two electrons occupying the same site. The Hubbard U parameter quantifies this repulsion as

$$\langle \hat{D}_U \rangle = \langle \Psi_G | \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} | \Psi_G \rangle = 4C^2 \quad (4.11)$$

The spin-spin correlation function represents the contribution of the exchange interaction in the

$$\langle \hat{D}_J \rangle = \langle \Psi_G | (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j - \frac{1}{4}) | \Psi_G \rangle = -1. \quad (4.12)$$

Intersite Coulomb correlation accounts for the Coulomb repulsion between electrons located on different sites

$$\langle \hat{D}_K \rangle = \langle \Psi_G | \hat{n}_i \hat{n}_j | \Psi_G \rangle = 2I^2. \quad (4.13)$$

Correlated-hopping correlation takes into account the energy associated with correlated hopping is

$$\langle \hat{D}_V \rangle = \langle \Psi_G | \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} (\hat{n}_{i\bar{\sigma}} + \hat{n}_{j\bar{\sigma}}) | \Psi_G \rangle = 16|CI| \quad (4.14)$$

In Fig. 4.5, the values of microscopic parameters multiplied by dynamic contributions for a hydrogen molecule, calculated as average values of operators for different interactions within the framework of the second quantization Hamiltonian, are presented. At $R = 0.5a_0$, the hopping energy contribution dominates, indicating strong electron mobility between sites. This is due to the significant overlap between atomic orbitals at this

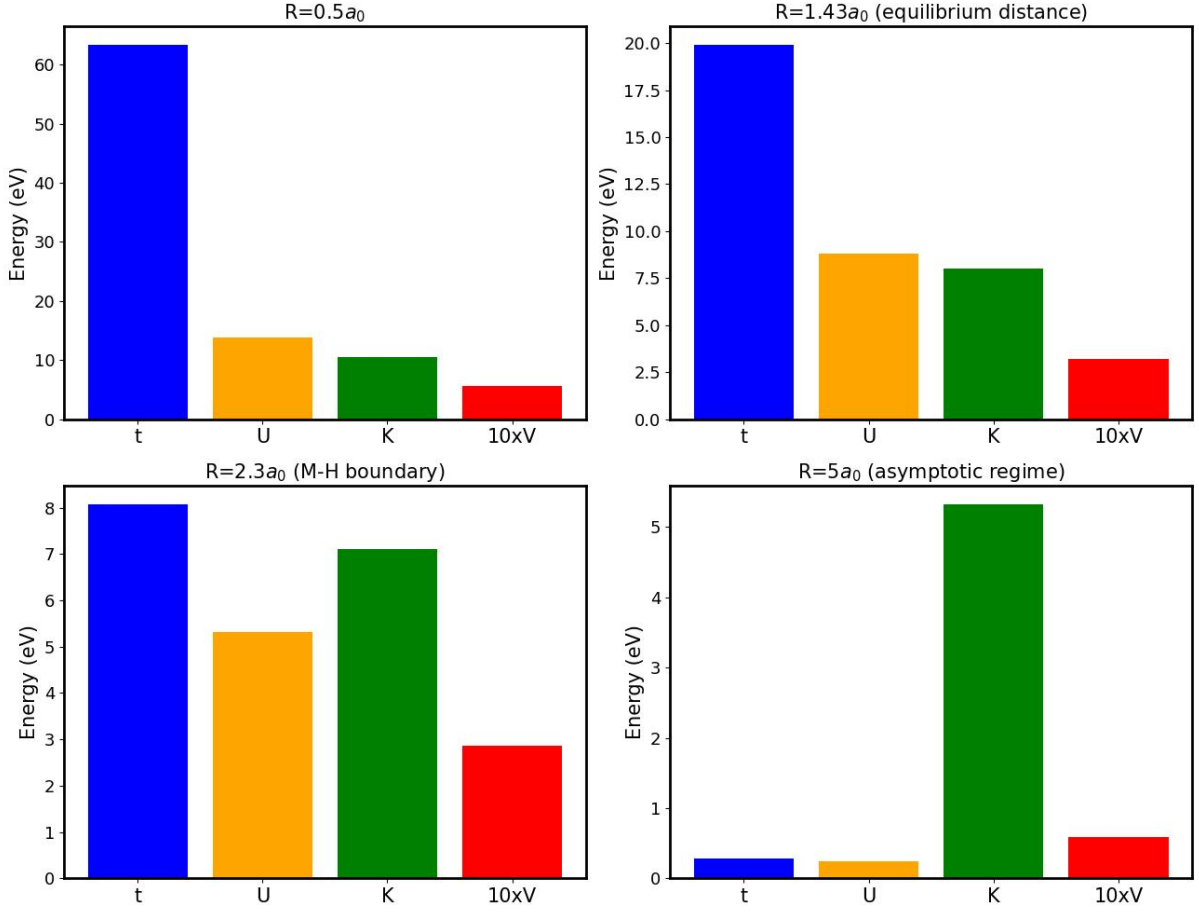


Figure 4.5: Bar charts presenting microscopic parameters values multiplied by dynamic contributions calculated as average values of operators for hopping t , Hubbard interaction U , interatomic Coulomb interaction K , and correlated hopping V multiplied by 10 for four different interatomic distance R values: $0.5a_0$, equilibrium distance $1.43a_0$, Mott-Hubbard criterion distance $2.3a_0$, and $5a_0$.

short distance. The values of U and K dynamic contributions are significantly lower than t , indicating that at very short distances, electron mobility dominates and electron correlation effects are less significant. Additionally, the dynamic contribution of correlated hopping, even when multiplied by 10, remains relatively low, suggesting that electron correlations have a smaller impact on hopping at this distance.

At the equilibrium distance $R = 1.43a_0$, the U and K dynamic contributions are approximately half of the hopping contribution. Meanwhile, the correlated hopping energy contribution remains relatively low, indicating that while correlations affect hopping, their impact is still smaller compared to direct hopping. These values suggest that at the equilibrium distance, electron mobility is balanced by repulsive interactions, maintaining molecular stability.

At the Mott-Hubbard boundary distance $R = 2.3a_0$, the hopping energy decreases further, indicating reduced electron mobility as the distance increases. The on-site Coulomb repulsion U remains crucial, showing that the energy cost of double occupancy is still important. The intersite Coulomb interaction K becomes more prominent, indicating stronger repulsion between electrons on different sites at this critical distance. The correlated hopping energy V , even when multiplied by 10, shows an increased impact, suggesting that electron correlations play a more substantial role at this boundary. These values indicate that at the Mott-Hubbard boundary, the system is at a crossover point, where electron mobility and electron-electron interactions balance each other, leading to a gradual transition between molecular and quasi-atomic.

In the asymptotic regime at $R = 5.0a_0$, the hopping energy is very low, reflecting minimal electron mobility due to the large distance. The on-site Coulomb repulsion U is less significant compared to shorter distances, indicating that the likelihood of double occupancy is low. The intersite Coulomb interaction K dominates, indicating significant repulsion between electrons on different sites due to the large separation. The hopping energy contribution V , as at smaller distances, is small. These values indicate that at large distances, the system behaves more like a system composed of single atoms, with electrons localized and intersite repulsions dominating.

4.4 Entanglement correlations as the complementary characterization of the chemical bond

The problem with correlation in molecular physics revolves around the difficulty of accurately and efficiently accounting for the interactions between electrons in a molecular system.

The exact wavefunction for the ground state of hydrogen molecule H_2 in the second quantization can be written in the form

$$|\Psi_G\rangle = \left(C(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger - \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) + I(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger + \hat{a}_{2\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) \right) |0\rangle, \quad (4.15)$$

where the covalent (C) and ionic (I) coefficients are written down. In this expression, the operator $\hat{a}_{i\sigma}^\dagger$, as it was stated earlier, represents the creation operator for a hydrogen atom on the i th site with spin σ . The indices 1 and 2 refer to the two hydrogen atoms in the H_2 molecule. The spin variables $\uparrow$ and $\downarrow$ represent the two possible spin orientations, up and down, respectively.

Our objective is to quantify entanglement using the provided two-particle wavefunction (Eq. 4.15). Therefore, we construct the density matrix

$$\rho = |\psi_G\rangle \langle \psi_G|. \quad (4.16)$$

To construct the density matrix, we take the tensor product of the wavefunction with its conjugate

$$\rho = |\Psi_G\rangle \langle \Psi_G| = (|\Psi_G\rangle) \otimes (\langle \Psi_G|) \quad (4.17)$$

Expanding the tensor product, we obtain

$$\begin{aligned} \hat{\rho} = & (C(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger - \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) + I(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger + \hat{a}_{2\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle) \\ & \otimes (C(\langle \hat{a}_{1\uparrow} | \langle \hat{a}_{2\downarrow} | - \langle \hat{a}_{1\downarrow} | \langle \hat{a}_{2\uparrow} | + I(\langle \hat{a}_{1\uparrow} | \langle \hat{a}_{1\downarrow} | + \langle \hat{a}_{2\downarrow} | \langle \hat{a}_{2\uparrow} |) \langle 0|), \end{aligned}$$

simplifying the expression, we have

$$\begin{aligned} \hat{\rho} = & C^2(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger - \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger)(\hat{a}_{1\uparrow} \hat{a}_{2\downarrow} - \hat{a}_{1\downarrow} \hat{a}_{2\uparrow}) \\ & + I^2(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger + \hat{a}_{2\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger)(\hat{a}_{1\uparrow} \hat{a}_{1\downarrow} + \hat{a}_{2\downarrow} \hat{a}_{2\uparrow}) \\ & + CI(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger - \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger)(\hat{a}_{1\uparrow} \hat{a}_{1\downarrow} + \hat{a}_{2\downarrow} \hat{a}_{2\uparrow}). \end{aligned} \quad (4.18)$$

To write the density matrix $\hat{\rho}$ in matrix form (ρ), we represent the states $|\uparrow_1\downarrow_2\rangle$, $|\downarrow_1\uparrow_2\rangle$, $|\uparrow_1\downarrow_1\rangle$, and $|\downarrow_2\uparrow_2\rangle$ in a chosen basis and construct the matrix elements accordingly.

Let us choose the basis $\{|\uparrow_1\downarrow_2\rangle, |\downarrow_1\uparrow_2\rangle, |\uparrow_1\downarrow_1\rangle, |\downarrow_2\uparrow_2\rangle\}$ to represent the density matrix. In this basis, the density matrix ρ can be written as a 4×4 matrix. Using the basis states, we can write the density matrix ρ in matrix form as

$$\rho = \begin{pmatrix} |C|^2 & 0 & IC & 0 \\ 0 & |C|^2 & 0 & IC \\ IC & 0 & |I|^2 & 0 \\ 0 & IC & 0 & |I|^2 \end{pmatrix} \quad (4.19)$$

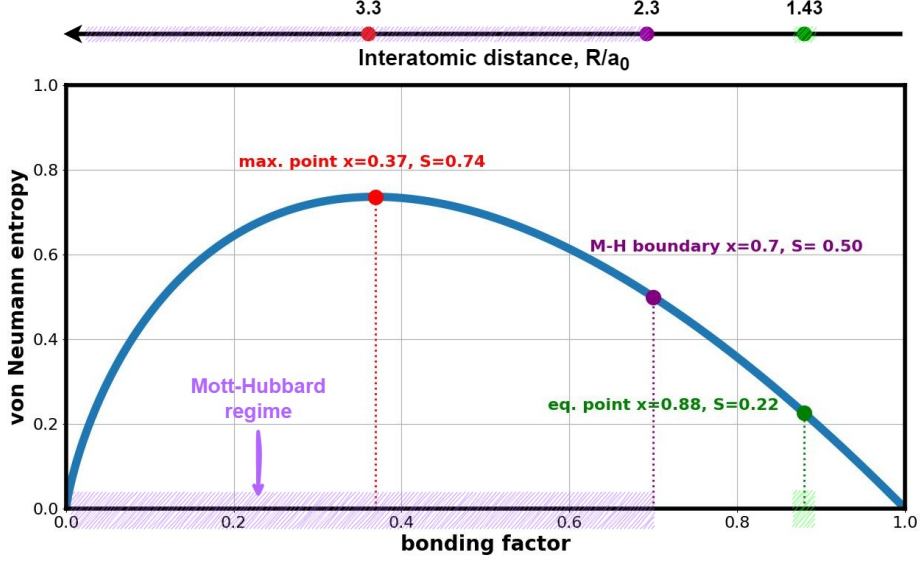


Figure 4.6: Illustration of the relation between the von Neumann entropy and the bonding factor in a molecular hydrogen system. The interatomic distance R/a_0 is indicated along the top axis, with key values marked: 3.3 maximal entropy point, 2.3 Mott-Hubbard point, 1.43 equilibrium distance. The Mott-Hubbard regime is highlighted in purple, indicating the transition from a conductive to an insulating state due to strong electronic interactions.

Subsequently, to determine the degree of entanglement we introduce, as above, the atomicity into the covalency factor (cf. (4.4)). In effect, we introduce a statistical admixture of atomicity into the pure two-particle quantum mechanical state. This procedure can be quantified further by calculating the two-particle von Neumann entropy

$$S = -\text{Tr}(\rho \ln \rho). \quad (4.20)$$

The entropy expresses the two-particle entanglement correlation in the mixed state expressed by the density matrix ((4.19)), readjusted in that manner.

The explicit form of the von Neumann entropy expressed via the bonding characteristics is

$$S = -2(\gamma_{cov} + \gamma_{ion}) \ln(\gamma_{cov} + \gamma_{ion}) = -2\gamma_{bond} \ln(\gamma_{bond}) \quad (4.21)$$

The entanglement determined in this way is plotted in Fig. 4.6 as a function of the bonding factor, i.e., combined $\gamma_{cov} + \gamma_{ion}$. The characteristic points like the equilibrium distance $R = R_{eq}$, the Mott-Hubbard boundary $R = R_{Mott}$, and the maximum entropy point are highlighted. The upper scale indicates the corresponding interatomic distances. A significant aspect of this diagram is that the maximum entropy appears near the point where the kinetic energy and interaction components are comparable, which is close to the Mott-Hubbard (M-H) crossover point. One can notice that the entire interaction dominated Mott-Hubbard regime is marked on the bonding factor axis. As it was stated in our recent work [39], these features allow us to consider entropy as a measure of *entanglement*

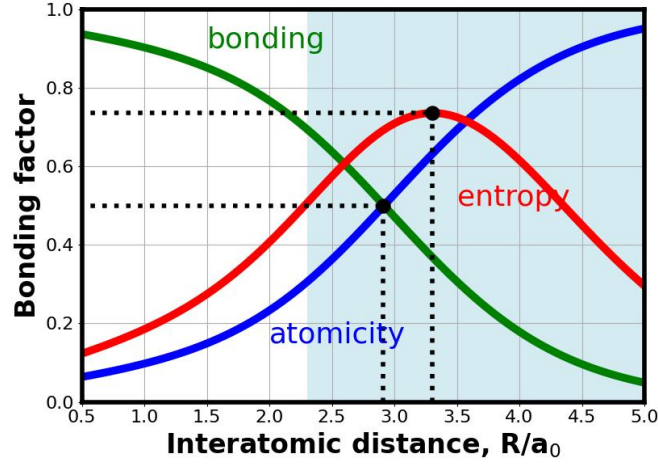


Figure 4.7: The relationship between the bonding factor, atomicity, and entanglement (von Neumann correlation entropy) is depicted as a function of interatomic distance. The shaded blue region represents the Mott-Hubbard regime.

correlations. There are two natural limit situations where entropy tends to zero. It is for the bonding factor equal to 0, it is happening where R is tending to zero, and where the bonding factor is equal to 1, which coincides with the situation where two atoms perfectly overlap.

Figure 4.7 illustrates the bonding characteristics we introduced as a complementary perspective to traditional energy considerations, plotted as a function of interatomic distance. Specifically, the point of maximum entanglement correlations is near where the bonding factor $\gamma_{cov} + \gamma_{ion}$ aligns with atomicity. This point can be viewed as critical for the transition from dominant single-particle bonding (characterized by the kinetic energy associated with electron hopping) to the interaction-dominated (M-H) regime. Although this point is relatively far from the equilibrium distance R_{eq} , it may play a crucial role in the molecular dissociation process in the presence of a catalyst. In summary, Figure 4.6 offers a comprehensive quantum description of a single chemical bond in diatomic molecules such as H_2 and similar systems [39].

4.5 Atomicity, covalency, and ionicity of excited states

As stated in Chapter 3, the diagonalization of the all-interactions Hamiltonian for the hydrogen molecule results in a solution involving four electronic states, even though only $1s$ orbitals are considered. This occurs because the trial basis includes six possible states differing in spin arrangement: three singlet states and one triplet state. An interesting question arises: how do the bonding factors differ for the four different states of the hydrogen molecule? Such a relation serves as a test of our concept of true covalency and atomicity.

All energies are listed in the panel of figures in Fig. 4.8 showing the bonding characteristics for one singlet ground state, two excited singlet states, and one triplet state of the hydrogen molecule. This figure also illustrates the atomicity, ionicity, and covalency for various ground and spin-excited states of the hydrogen molecule as functions of the interatomic distance R . The energy expressions for these states include contributions from atomic kinetic energy, hopping interaction, Coulomb interaction, interatomic interaction and exchange terms.

Starting from the bottom-left panel, one can see that it shows the bonding characteristics for the ground state energy. As discussed earlier, the covalent contribution dominates at $R = R_{bond}$. However, there is a small admixture of atomic contribution, indicating that in 15% of the cases, the two-particle wavefunction behaves like the wavefunction of two separated atoms. The ionic contribution is more noticeable than the atomic one, but as R increases, both covalent and ionic characters vanish, while the atomic character persists. The proper eigenvector in the second quantization can be written in the following form

$$|6\rangle = C \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle - I \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger + \hat{a}_{2\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger \right) |0\rangle, \quad (4.22)$$

where C and I as earlier denote covalent and ionic factors. The transition from covalent-dominated bonding to atomic state is consistent with the intuitive picture resulting from the interpretation of the behavior of the binding energy curve, where in the limit $R \rightarrow \infty$ the molecule dissociate into two individual atoms.

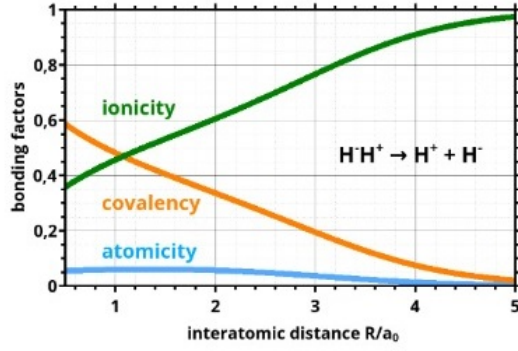
The top-left panel represents the singlet state. In this case, ionicity contribution is dominant. The contribution of ionicity in this case is significantly smaller than for the ground state, which is due to the nature of the wave function. As the interatomic distance increases, the covalency and atomicity as expected approach zero whereas ionicity reaches a value of unity. The correspondent state is

$$|5\rangle = C' \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle + I' \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger + \hat{a}_{2\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger \right) |0\rangle, \quad (4.23)$$

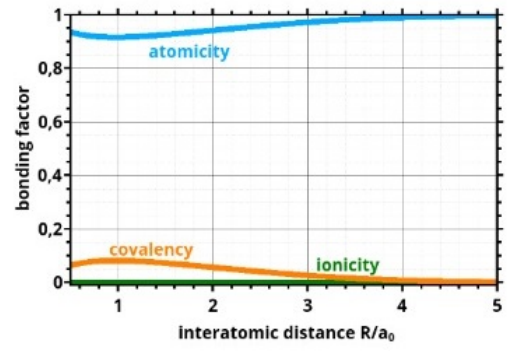
where in this case there new coefficients C' and I' represent covalent and ionic factor, with $C' = 4(t + V)/\sqrt{2D(D - U + K)}$ and $I' = \sqrt{(D - U + K/2D)}$. As shown in Fig. 3.6, this state has a shallow minimum at $R = 3.5a_0$. A molecule excited to this state has a metastable ionic character. Then in the limit of infinite R dissociation occurs, but unlike that in the ground state, it now results in H^+ and H^- ions rather than two neutral atoms.

The top-right panel also depicts an excited singlet state. In this state, atomicity is shown to be the dominant characteristic across the range of interatomic distances presented. Covalency and ionicity remain minimal, suggesting that the bonding in this excited state is predominantly characterized by atomicity. Three generated eigenvectors one can write as

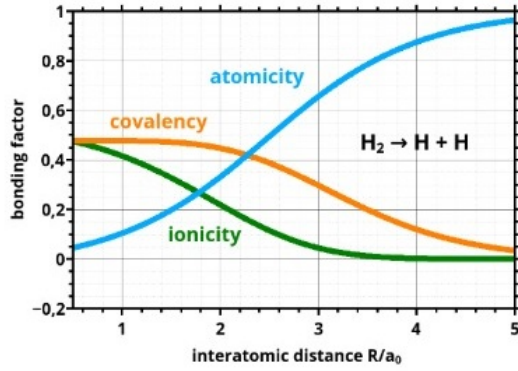
singlet $E_1 = 2\epsilon + (U+K)/2 + J + 2D$



singlet $E_5 = 2\epsilon + K - J$



singlet $E_1 = 2\epsilon + (U+K)/2 + J - 2D$



triplet $E_2 = E_3 = E_4 = 2\epsilon + U - J$

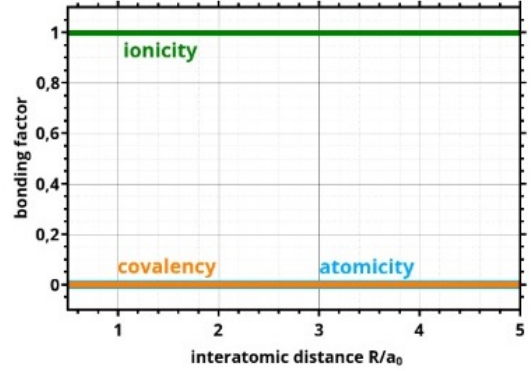


Figure 4.8: The atomicity, ionicity, and covalency for various ground and spin-excited states of the hydrogen molecule (H_2) as functions of the interatomic distance R . The energy expressions for these states include contributions from kinetic energy, Coulomb interaction, and exchange terms.

$$|1\rangle = \hat{a}_{1\uparrow}^\dagger \hat{a}_{2\uparrow}^\dagger |0\rangle, \quad (4.24)$$

$$|2\rangle = \hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger |0\rangle, \quad (4.25)$$

$$|3\rangle = \frac{1}{\sqrt{2}} \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle. \quad (4.26)$$

In this case, covalency, ionicity and atomicity depend only on mixing parameters.

State $|1\rangle$ represents a configuration where both electrons are in a spin-up state. This kind of configuration typically does not contribute to the covalent bond because it does not allow for the formation of paired electrons with opposite spins, which is a prerequisite for strong covalent bonding.

State $|2\rangle$ is characterized by the fact that one electron is in the spin-up state and one is in the spin-down state. It partially allows for covalent bonding, but given that the spins are not paired in the same orbital, the bonding is not as strong as in the fully paired configuration.

State $|3\rangle$ is a superposition state where the electrons are paired in a symmetric combination. This configuration is characteristic of an excited singlet state, where the electrons are paired but not in the lowest energy configuration. This can lead to a situation where

atomicity (the characteristic of being like separate atoms) is more dominant compared to strong covalent bonding.

The bottom-right panel represents a triplet state. This panel shows that the ionicity is equal to one while covalency and atomicity remain zero. The eigenvector for this state is as follows

$$|4\rangle = \frac{1}{\sqrt{2}} (\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger - \hat{a}_{2\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger) |0\rangle \quad (4.27)$$

As in the previous case, bonding factors are only functions of mixing parameters.

One can see that in this wavefunction there is no covalent or atomic admixture. This state is also unstable, which leads to the conclusion that the molecule in this state is a kind of resonant structure between bound and free ionic forms.

Not only the wavefunction can be analyzed in the context of bonding characteristics, but energy can also be used for this purpose. Let us consider two similar cases of singlets: the ground state singlet and the excited singlet, where the energy differs only by a factor of $2D$. In the first case, the energy contains a $+2D$ factor, and in the latter case, a $-2D$ factor.

The addition of $2D$ to the energy term increases the contribution of the ionic interactions (related to U and K). As D is positive, adding it increases the separation of charges, leading to a more ionic character where the molecule dissociates into ions H^+ and H^- .

Covalent State (bottom left): The subtraction of $2D$ from the energy term reduces the contribution of the ionic interactions, enhancing the covalent nature where the electrons are more shared between the atoms. This leads to a lower energy state typical of covalent bonds, where the molecule dissociates into neutral atoms ($H + H$).

In the case of the singlet in the top-right side of the panel in Fig. 4.8, the atomic character based on the energy is quite obvious. The energy equation includes the term K , which generally represents interatomic Coulomb interaction promoting atomicity, and $-J$, which is an exchange interaction term that tends to stabilize the singlet state and is not present in the wavefunction. The presence of K and $-J$ without any direct dependence on the intraatomic Coulomb interaction term U indicates that this state is more likely to retain atomic characteristics rather than form strong covalent or ionic bonds. The higher atomicity in the graph aligns with this, as the energy expression supports a state where atoms remain relatively independent.

Chapter 5

Summary and perspectives

5.1 Summary

The aim of this Thesis was to investigate diatomic molecular systems, using methods developed and applied in our group for systems with strongly correlated electrons (EDABI). In our opinion, this approach contributes to the ongoing discussion on the fundamentals of quantum chemistry, particularly concerning chemical bonding, and the basics of quantum mechanics, especially the entanglement of two fermions. The scope of this work includes the numerical implementation of the EDABI method, based on the combined language of first- and second-quantization as applied to diatomic molecular systems (H_2^+ , H_2^- , LiH , HeH^+). The dissertation also encompasses the analysis and interpretation of the characteristics of chemical bonding, based on the exact solution of extended the Heitler-London model for the H_2 molecule, focusing particularly on the dynamic interplay of the true covalency, atomicity, and ionicity. Furthermore, we explore the dynamic contributions to the ground state energy, coming from various terms in the full two-atomic Hamiltonian as a function of interatomic distance. The research highlights the correspondence between the behavior of molecular systems and nanosystems at the onset or crossover of the Mott-Hubbard transformation. Additionally, the work involved a comparative analysis of results obtained from the EDABI method with those from state-of-the-art quantum chemistry methods, such as Configuration Interaction (CI) and Hartree-Fock (HF) approaches. Through this investigation, the dissertation aims to provide a deeper and complementary understanding of the fundamental properties of chemical bonds in molecular systems, bridging the gap between molecular and condensed matter physics, as well as, offering new insight into the true covalency, atomicity, and ionicity of the chemical bond.

5.2 Perspectives

Our original contribution focused on the properties of chemical bonding via a combined approach of first- and second-quantization, specifically addressing the problem of true covalency, atomicity, and ionicity. In our opinion, this merely initiates the discussion on these problems. Apart from the prevailing numerical challenges, such as a need for more efficient methodological implementations, and analytical challenges, we believe that overcoming these obstacles could unveil numerous opportunities. These potential advancements are outlined in the following future perspectives:

1. The EDABI method has been successfully applied to simple diatomic molecules. Future research could extend this method to larger and more complex molecular systems, including polyatomic molecules or nanosystems. This should result in deeper insights into the nature of chemical bonding in more intricate situations.
2. Machine learning algorithms could be integrated with the EDABI method to predict and analyze the properties of molecular systems more efficiently. This combination could lead to the discovery of new materials and molecules with tailored properties, accelerating the pace of research in fields such as drug design and materials science.
3. The theoretical findings of this thesis could be experimentally validated using advanced spectroscopic techniques and high-resolution microscopy. Collaborations with experimental chemists could help verify the predictions and potentially lead to the development of new experimental protocols to observe the predicted phenomena.
4. The concepts of true covalency, atomicity, and ionicity could be explored in biological molecules and systems, especially such as appear in hydrogen bonding. Preliminary work on the hydrogen bonding in the case of DNA is underway.

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Many-particle covalency, ionicity, and atomicity revisited for a few simple example molecules

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Abstract

We analyze two-particle binding factors of H_2 , LiH , and HeH^+ molecules/ions with the help of our original exact diagonalization *ab initio* approach. The interelectronic correlations are taken into account rigorously within the second quantization scheme for restricted basis of renormalized single-particle wave functions, i.e., with their size readjusted in the correlated state. This allows us to determine the many-particle covalency and ionicity factors in a natural and intuitive manner in terms of the microscopic single-particle and interaction parameters, also determined within our method. We discuss the limitations of those basic characteristics and introduce the concept of atomicity, corresponding to the Mott and Hubbard criterion concerning localization threshold in many-particle systems. This addition introduces an atomic ingredient into the electron states and thus removes a spurious behavior of covalency with the increasing interatomic distance, as well as provides a more complete physical interpretation of bonding.

Keywords: atomicity in molecules, Mottness, resonant covalency, electron correlations, EDABI method

(Some figures may appear in colour only in the online journal)

1. Introduction

Determination of the microscopic nature of chemical bonding has been regarded as a problem of fundamental significance since the advent of quantum chemistry and solid state physics [1–3]. The qualitative classification of the valence-electrons state character as *covalent*, *ionic* or *atomic* helps to rationalize their overall features and select a detailed approach to analyze their detailed electronic properties. In this respect, the role of interactions and associated with them interelectronic

correlations is crucial in discussing the evolution of bonding from either atomic or ionic character to predominantly covalent or band states of valence electrons. The many-electron approaches, such as configuration interaction (CI) [4] and others [5, 6], are particularly well suited for this task.

In this work we follow a different route and employ exact diagonalization *ab initio* (EDABI) method, combining the second-quantization formulation of quantum many-particle Hamiltonian with a concomitant readjustment of the single-particle wave functions in the correlated state of the system. This allows us to reinterpret some of the chemical bonding characteristics using concepts originating from condensed-matter physics, such as Mott–Hubbard localization. EDABI has been formulated in our group some time ago [7–9] and analyzed extensively in the context of correlated states in small clusters and one-dimensional solid-state systems. Apart from

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providing rigorous description of selected properties, EDABI has supplied us with the evolution from the atomic- to a coherent-metallic state with decreasing interatomic distance. Also, modeling the metallization of molecular hydrogen solid has revealed a series of discontinuous first-order Mott-type transitions as a function of applied pressure [10–12]. The explicit question we would like to address here is to what extent the concepts essential extended to lattice quantum systems, such a *Mottness* [13, 14], may also be qualitatively applicable to finite molecular systems. Answering this question forced us to reanalyze the meaning of the two-particle covalency and related to it ionicity factors by starting from an analytic form of many-particle wave function. We suggest that such analysis may be useful in practical treatment of bonding, here carried out in two-atom–molecule situation, to make the discussion analytic and thus provide a degree of clarity.

The structure of the paper is as follows. In section 2 we summarize briefly the EDABI approach. In section 3 we reanalyze the bonding in H_2 , HeH^+ , and LiH systems. We also discuss there validity of the concept of atomicity—*Mottness*, with the help of which we single out the *resonant covalency* and atomicity factors. This discussion offers a resolution of the longstanding paradox of the increasing covalency with the increasing interatomic distance. Finally, in sections 4 and 5 we overview our approach. Formal details and tabulated values of the calculated microscopic parameters as a function of interatomic distance are provided in appendices A and B.

2. EDABI method and many-particle bonding

The EDABI method has been proposed by us and formulated in detail earlier [7, 9]. Below, we provide a brief summary of its main features, as this should be helpful in grasping the essence of our approach which will be needed in a subsequent interpretation of the results regarding many-particle covalency and ionicity, as well as the concept introduced by us of atomicity.

The starting point is the Hamiltonian containing all pairwise interactions in the second-quantized form is

$$\begin{aligned} \hat{\mathcal{H}} = & \epsilon_a \sum_i \hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \\ & + \frac{1}{2} \sum_{ij} K_{ij} \hat{n}_{i\sigma} \hat{n}_{j\sigma'} - \frac{1}{2} \sum_{ij} J_{ij}^H \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j - \frac{1}{4} \hat{n}_i \hat{n}_j \right) \\ & + \frac{1}{2} \sum_{ij} J'_{ij} (\hat{a}_{i\uparrow}^\dagger \hat{a}_{i\downarrow}^\dagger \hat{a}_{j\downarrow} \hat{a}_{j\uparrow} + \text{H.c.}) \\ & + \frac{1}{2} \sum_{ij} V_{ij} (\hat{n}_{i\sigma} + \hat{n}_{j\sigma}) (\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + \text{H.c.}) + \mathcal{H}_{\text{ion-ion}}, \quad (1) \end{aligned}$$

where H.c. denotes the Hermitian conjugation, $\hat{a}_{i\sigma}$ ($\hat{a}_{i\sigma}^\dagger$) are fermionic annihilation (creation) operators for state i and spin σ , $\hat{n}_{i\sigma} \equiv \hat{a}_{i\sigma}^\dagger \hat{a}_{i\sigma}$, and $\hat{n}_i \equiv \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} \equiv \hat{n}_{i\sigma} + \hat{n}_{i\bar{\sigma}}$. The spin operators are defined as $\hat{S}_i \equiv \frac{1}{2} \sum_{\alpha\beta} \hat{a}_{i\alpha}^\dagger \sigma_i^{\alpha\beta} \hat{a}_{i\beta}$ with σ_i representing

Pauli matrices. The Hamiltonian contains the atomic and hopping parts ($\propto \epsilon_a$ and t_{ij} , respectively), the so-called Hubbard term $\propto U$; representing the intra-atomic interaction between the particles on the same atomic site i with opposite spins, the direct intersite Coulomb interaction $\propto K_{ij}$, Heisenberg exchange $\propto J_{ij}^H$, and the two-particle and the correlated hopping terms ($\propto J'_{ij}$ and V_{ij} , respectively). The last term describes the ion–ion Coulomb interaction which is adopted here in its classical form.

We now proceed to definition of two-particle bonding in general situation and within the second-quantization representation. The N -particle state, $|\Psi_N\rangle$, may be expressed in terms of the N -particle wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ and the corresponding field operators $\hat{\Psi}(\mathbf{r}_1), \dots, \hat{\Psi}(\mathbf{r}_N)$ as

$$|\Psi_N\rangle = \frac{1}{\sqrt{N!}} \int d^3r_1 \dots d^3r_N \Psi_N(r_1, \dots, r_N) \times \hat{\Psi}_1^\dagger(r_1) \dots \hat{\Psi}_N^\dagger(r_N) |0\rangle, \quad (2)$$

with $|0\rangle$ being the universal vacuum state in the Fock space (for pedagogical exposition see, e.g., [15]). Here we employ a short-hand notation $r_i \equiv (\mathbf{r}_i, \sigma_i)$, where $\sigma_i = \pm 1$ is the spin quantum number. We can revert this relation to determine the wave function $\Psi_N(r_1, \dots, r_N)$, namely

$$\Psi_\alpha(r_1, \dots, r_N) = \frac{1}{\sqrt{N!}} \langle 0 | \hat{\Psi}_1(r_1) \dots \hat{\Psi}_N(r_N) | \lambda_\alpha \rangle, \quad (3)$$

where $|\lambda_\alpha\rangle$ is the eigenstate for which the wavefunction Ψ_α is explicitly determined. For spin-conserving interaction, $\alpha = (\sigma_1, \sigma_2, \dots, \sigma_N)$ is fixed N -spin-configuration. In effect, we determine $|\lambda_\alpha\rangle$ states around ground eigenstate $|\lambda_\alpha\rangle \equiv |\lambda_{\min}\rangle$. Hamiltonian (1) is used to obtain the eigenstates which for two-electron H_2 system are discussed analytically in appendix A.

Since we focus explicitly on the two-site systems, the set of microscopic parameters (ϵ_a , t , U , K , J , J' , and V) is defined through integrals of orthogonalized single particle basis functions, $\{w_i(\mathbf{r})\}$, used next to define the field operators in turn needed to construct the Hamiltonian (1). They are defined briefly first [7, 9], whereas the values of the microscopic parameters are defined in appendix B, starting from the nonorthogonal basis set of adjustable Slater functions. Namely, the orthogonalized atomic (Wannier) orbitals for H_2 molecule the $1s$ are defined via Slater orbitals $\{\psi_i(\mathbf{r})\}$ in the usual manner

$$w_{i\sigma}(\mathbf{r}) = \beta[\psi_{i\sigma}(\mathbf{r}) - \gamma\psi_{j\sigma}(\mathbf{r})], \quad (4)$$

where $\sigma \pm 1$ is spin quantum number $i \neq j = 1, 2$, and the coefficients β and γ take the form

$$\begin{cases} \beta = \frac{1}{\sqrt{2}} \sqrt{\frac{1 + \sqrt{1 - S^2}}{1 - S^2}}, \\ \gamma = \frac{S}{1 + \sqrt{1 - S^2}}, \end{cases} \quad (5)$$

so that $\beta^2 + \gamma^2 = 1$. The Slater orbitals $\psi_i(r) \equiv \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha(\mathbf{r} - \mathbf{R}_i))$, with α being the inverse size of the orbital, are to be readjusted during the ground-state-energy minimization in the *correlated state*. Optimization over parameter α is motivated by the circumstance that the selected single-particle basis $\{\psi_i(\mathbf{r})\}$ is never complete in the quantum mechanical sense and thus such a procedure allows for a better estimate of the ground-state energy. This allows for the orbital-size adjustment in the interacting environment of remaining particles. In brief, the standard procedure of determining the quantum-mechanical state of the system is inverted in the sense that we first diagonalize many-particle Hamiltonian for fixed values of the microscopic parameters and, subsequently, readjust the wave function (inverse size, α^{-1}) in a recurrent fashion. The whole procedure is schematically illustrated by a flowchart composing figure 1.

The selected a single-particle basis for H_2 is composed of four orthogonalized wave functions with indices $i = 1, 2$ enumerating hydrogen atoms and $\sigma = \pm 1$ for each i . Thus, the truncated field operator takes the form

$$\hat{\Psi}(\mathbf{r}) = \sum_{i=1}^2 w_i(\mathbf{r}) \chi_{\sigma}(\mathbf{r}) \hat{a}_{i\sigma}. \quad (6)$$

In that situation, the two-particle wave function is defined in accordance with equation (3), namely

$$\Psi_{\alpha}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \langle 0 | \hat{\Psi}_1(\mathbf{r}_1) \hat{\Psi}_2(\mathbf{r}_2) | \lambda_{\alpha} \rangle, \quad (7)$$

where $|\lambda_{\alpha}\rangle$ is the eigenstate (expressed in second quantization representation). Note that this method of approach allows to determine both the ground-state and the lowest excited states for a single optimal value of α .

Note that here the subscripts 1 and 2 of $\hat{\Psi}(\mathbf{r})$ contain both site and spin indices for brevity of notation. Parenthetically, one may generalize the above definition to the case of multiple (n) bonds (with $n \geq 1$) as

$$\Psi_a(\mathbf{r}_1, \dots, \mathbf{r}_{2n}) = \frac{1}{\sqrt{2n!}} \langle 0 | \prod_{i=1}^n \hat{\Psi}_i(\mathbf{r}_i) \prod_{j=n+1}^{2n} \hat{\Psi}_j(\mathbf{r}_j) | \lambda_{\alpha}^{(n)} \rangle. \quad (8)$$

In this manner the double ($n = 2$) and triple ($n = 3$) bonds can be defined, albeit numerically only and in more complex situations, e.g., in the case of carbon–carbon bonds. This scenario is not addressed here. Instead, we focus on the covalency and ionicity, as well as introduce *atomicity* + *covalency* factor, all for selected two-electron systems. However, we discuss first the inherent paradox of the increasing covalency with the increasing interatomic distance.

3. Covalency, ionicity, and atomicity on examples

3.1. Covalent bonding and ionicity in H_2 case

With the help of analysis presented in appendix A for the H_2 case, one can write down explicitly the two-electron wave function in the ground state for H_2 molecule ($n = 1$ case). The lowest-energy spin-singlet state is of the form

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{2(t+V)}{\sqrt{2D(D-U+K)}} \Psi_c(\mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2} \sqrt{\frac{D-U+K}{2D}} \Psi_i(\mathbf{r}_1, \mathbf{r}_2), \quad (9)$$

where the covalent (Ψ_c) and ionic (Ψ_i) components, read

$$\Psi_c(\mathbf{r}_1, \mathbf{r}_2) = [w_1(\mathbf{r}_1)w_2(\mathbf{r}_2) + w_1(\mathbf{r}_2)w_2(\mathbf{r}_1)] \times [\chi_{\uparrow}(\mathbf{r}_1)\chi_{\downarrow}(\mathbf{r}_2) - \chi_{\downarrow}(\mathbf{r}_1)\chi_{\uparrow}(\mathbf{r}_2)], \quad (10)$$

$$\Psi_i(\mathbf{r}_1, \mathbf{r}_2) = [w_1(\mathbf{r}_1)w_1(\mathbf{r}_2) + w_2(\mathbf{r}_1)w_2(\mathbf{r}_2)] \times [\chi_{\uparrow}(\mathbf{r}_1)\chi_{\downarrow}(\mathbf{r}_2) - \chi_{\downarrow}(\mathbf{r}_1)\chi_{\uparrow}(\mathbf{r}_2)], \quad (11)$$

with

$$D \equiv \sqrt{(U-K)^2 + 16(t+V)^2}. \quad (12)$$

The ratio of the coefficients in (9) provides us with the relative ratio of covalency to ionicity in the ground-state spin-singlet configuration. The spin-singlet part is the same in both equations (10) and (11). Explicitly, the covalency and ionicity coefficients (factors) are defined as

$$\gamma_c = \frac{16(t+V)^2}{16(t+V)^2 + (D-U+K)^2}, \quad (13)$$

and

$$\gamma_i = \frac{(D-U+K)^2}{16(t+V)^2 + (D-U+K)^2}, \quad (14)$$

respectively, so that the condition $\gamma_i + \gamma_c = 1$ holds. The factor γ_i asymptotically approaches zero in the limit of large interatomic distance ($R \rightarrow \infty$), as expected. However, $\gamma_c \rightarrow 1$ for $R \rightarrow \infty$ which represents an *unphysical* behavior [16–18]. This last feature will be discussed in detail below.

The obtained formulas are interpreted as follows. First, the coefficients γ_c and γ_i in the wave function (9) depend on all the interactions which are present in (1), i.e., they contain the effects electronic correlations. Second, the wave functions (10) and (11) take formally the Heitler–London form, but they are self-consistently optimized in the correlated state (their size α^{-1} is adjustable). Thus, the present formulation in its simplest form contains a semiquantitatively correct behavior in the large- R limit, as is demonstrated explicitly in figure 2.

In figure 2, we display the H_2 binding energy and have compared our EDABI calculated value with the results of CI and restricted Hartree–Fock (RHF) analysis. Note difference between the results for small $R < R_{\text{bond}}$ (at minimum), as EDABI method provides slightly lower energies compared to those of full CI. This behavior should not influence the subsequent discussion in the large- R limit, which concerns us mainly here. Nonetheless, it is worth noting both CI and EDABI are variational approaches and perhaps our optimization of the wave-function size at small R is as important as the inclusion of the higher excited states. The binding energy is defined as $E_{\text{bind}} = \lambda_5 - 2E_{\text{H}}$ (λ_5 is defined in appendix A), where $E_{\text{H}} = -1$ Ry is the energy of $1s$ state in atomic hydrogen. Next, we define the bonding and ionicity as the corresponding ratios of coefficients in equation (9), cf figure 3. We note

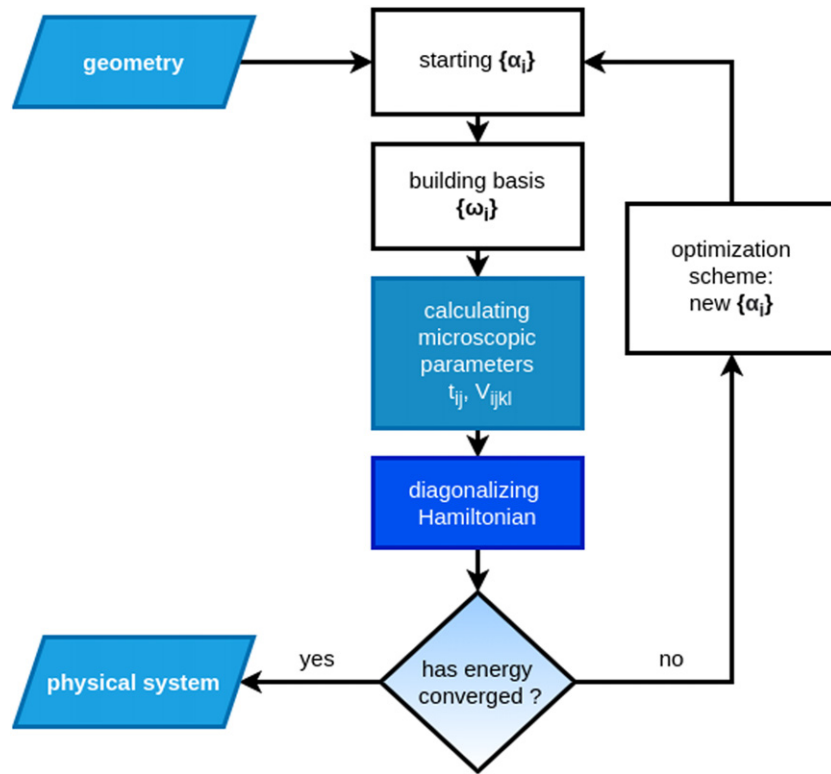


Figure 1. Flowchart of the EDABI method. The method is initialized by selection of a trial single-particle basis of wave functions, $\{w_i(\mathbf{r})\}$, and subsequent diagonalization the resulting many-particle Hamiltonian. Optimization of the single-particle states leads to an explicit determination of the trial-wavefunction parameters, microscopic interaction and hopping parameters, ground-state energy, and explicit many-particle wavefunction, all in the correlated interacting state. For detailed discussion see main text.

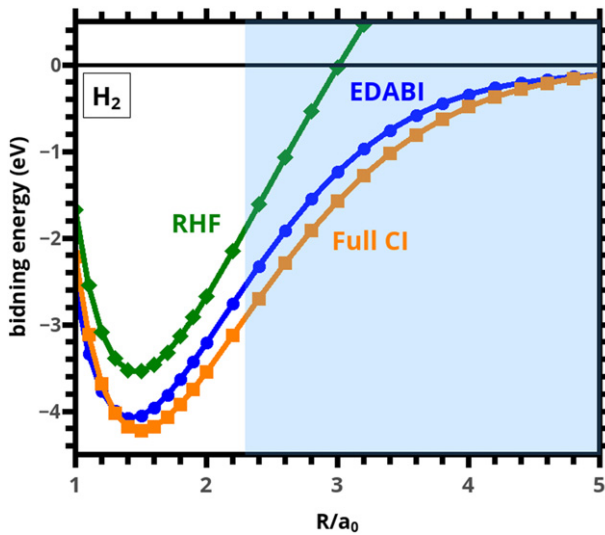


Figure 2. The H_2 binding energy versus relative interatomic distance, calculated within EDABI and compared with RHF and full CI method. a_0 is the Bohr radius. EDABI yields slightly lower energy than full CI calculation at very small interatomic distance, R ; this difference does not alter the main point of our qualitative discussion.

that the covalency increases with the increasing interatomic distance at the expense of ionicity. However, this apparent inconsistency ignores the possibility of incipient atomicity of the *Mott–Hubbard type*, i.e., the tendency toward localization of electrons on parent atoms with increasing R (called briefly

the Mottness). The Mott-type criterion for the localization of electron on H^+ ion (i.e., formation of renormalized atomic states) takes the form $2|t + V|/(U - K) = 1$. This condition expresses the fact that the of bare kinetic energy is then equal to the effective repulsive Coulomb interaction ($U - K$). In the strong correlation limit, the ratio is below unity, meaning this repulsive interaction becomes predominant (note that in the strict atomic limit, $t + V \equiv 0$ whereas $U - K = 1.25 \text{ Ry}$ then). The regime of strong-correlations (Mottness) is marked explicitly in figures 3 and 4. It specifies a gradual evolution toward the atomic state. Namely, the shaded area should be regarded as the regime with steadily increasing atomicity of the electronic states with increasing R . Thus, the question of unphysically increased covalency for $R > R_{\text{Mott}}$ is resolved in a natural manner as within the shaded area the covalency, γ_c , is composed of a sum of true (resonant) covalency $\bar{\gamma}_c \rightarrow 0$ and atomicity $\gamma_a \rightarrow 1$ as $R \rightarrow \infty$ (see the discussion below).

3.2. Correlation effects and incipient Mottness

The general meaning of the Mott (or Mott–Hubbard) effects is as follows. In condensed-matter physics the criterion takes the form of $U \simeq W$ [20], where $W \equiv |\sum_{j(i)} t_{ij}|$ is the bare band-width. The transition takes the form of often discontinuous metal–insulator transition for odd integer number of relevant valence electrons per atom. In molecular system, such as H_2 , the HOMO–LUMO splitting $\simeq U - K$ must overcome the

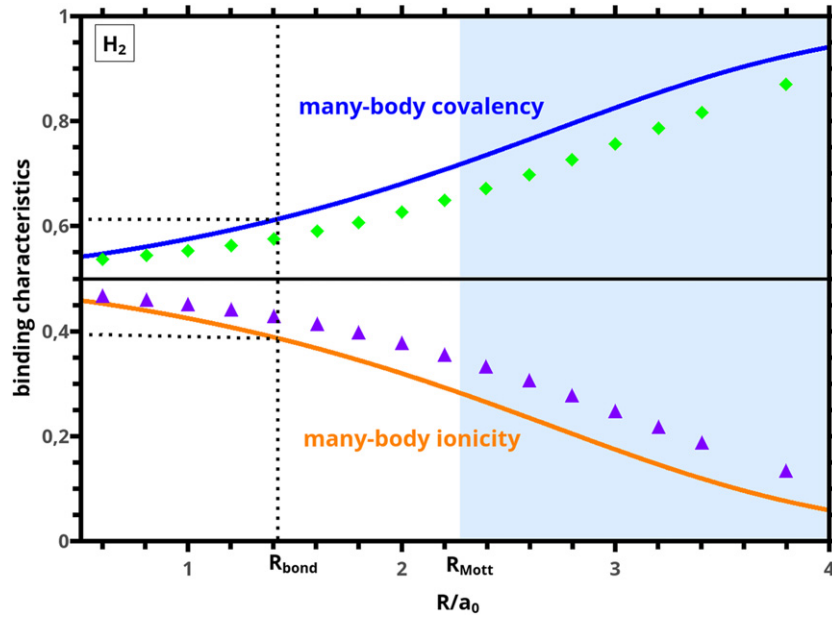


Figure 3. Two-particle covalency vs corresponding ionicity for H_2 molecule, calculated within EDABI method and compared with the results of reference [19]. Shaded regime marks a gradual evolution toward *atomicity*, as determined from the Mott–Hubbard criterion (see in the main text). Vertical dotted line marks equilibrium interatomic distance, whereas the horizontal dotted lines illustrate the dominant character of the covalency in that state (with the ratio $r = 1.43 \sim 2 : 1$).

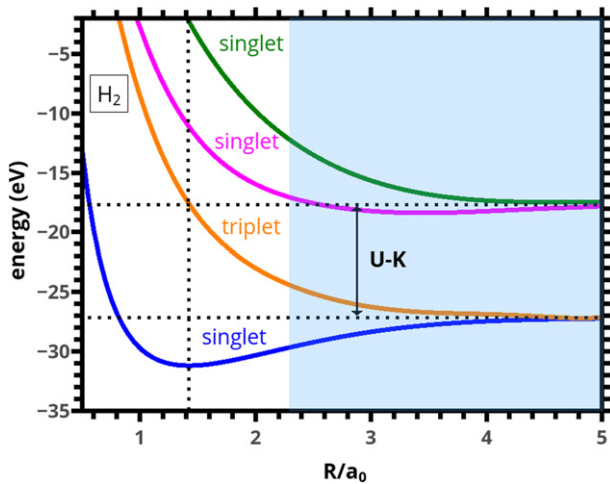


Figure 4. The lowest energy levels composed of three singlet and three triplet states, with the marked Mott regime and associated with it strong-correlation limit (shaded area). The scale $U - K$ represents the effective repulsive Coulomb interaction between electrons, i.e., the HOMO–LUMO splitting. The atomic character of the states increases with the increasing interatomic distance R .

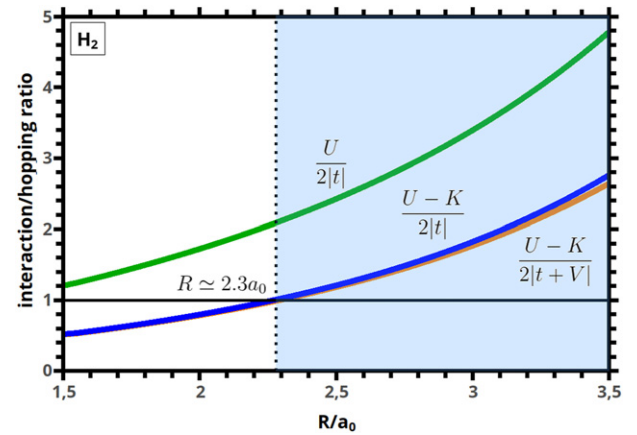


Figure 5. Characteristics of the H_2 state. The condition $(U - K)/(2|t + V|) = 1$ is the so-called Mott or Mott–Hubbard criterion for atomic localization which, in turn, determines the critical interatomic distance $R/a_0 \simeq 2.3$, representing the border of hatched area in figures 3 and 4. The atomic character of electron wave function becomes gradually enhanced with increasing $R > R_{\text{Mott}}$. The remaining curves have a supplementary character (see main text).

effective interatomic hopping amplitude $W = 2|t|$. For Hamiltonian (1), the Mott–Hubbard criterion takes then the form $r \equiv (U - K)/(2|t + V|) \simeq 1$ so that both the correlated hopping and intersite Coulomb interaction contribute, in addition to t and U . In the present situation, the criterion separates only qualitatively the regime of strong correlations ($r \geq 1$) from that with moderate to weak correlations ($r < 1$). Various versions of the criterion have been shown in figure 5, depending on the theoretical model selected. Namely, the uppermost

curve (in green) provides the criterion for the Hubbard model, which does not yield any Mottness point in the present situation. On the other hand, both the model with $V = 0$ and the full model (represented by the starting Hamiltonian (1)), are almost identical and yield the critical interatomic distance for localization $R = R_{\text{Mott}} \simeq 2.3a_0$, i.e., well above the $R_{\text{bond}} \simeq 1.43a_0$. Note also that even for equilibrium distance $R = R_{\text{bond}}$ the hopping/interaction ratio is about ~ 0.5 , i.e., the electrons are moderately correlated.

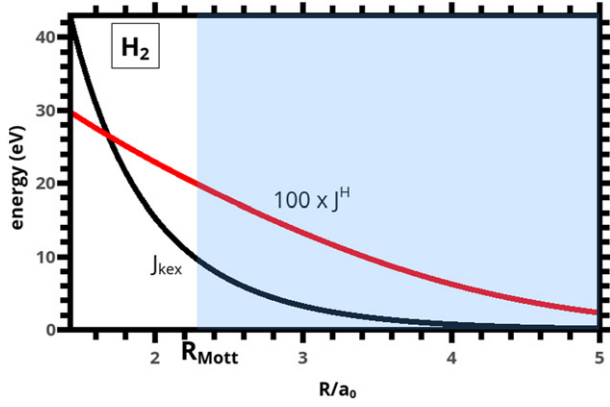


Figure 6. The antiferromagnetic kinetic exchange (superexchange) integral, J_{kex} , calculated as a function of interatomic distance within EDABI approach. Superexchange dominates over its ferromagnetic Heisenberg correspondent, J^H , and provides the justification for the molecule spin-singlet configuration. The kinetic exchange originates from virtual resonant hopping of the electron between the atoms [21].

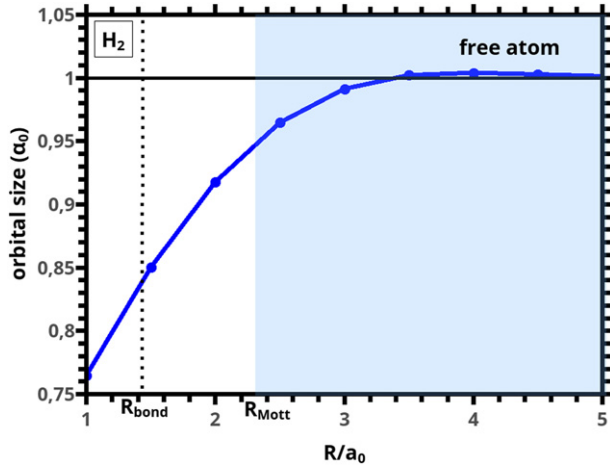


Figure 7. Renormalized $1s$ orbital size α^{-1} (in Bohr units a_0) vs relative interatomic distance for the H_2 molecule. Note that after crossing the Mott–Hubbard point $R = R_{\text{Mott}}$, α^{-1} approaches rapidly its atomic-limit value $\alpha^{-1} = a_0$.

To complete the picture, we have also plotted in figure 6 the antiferromagnetic kinetic-exchange integral $J_{\text{kex}} = 4(t + V)^2/(U - K)$ versus the direct (Heisenberg) ferromagnetic value J^H , both as a function of relative distance R/a_0 . The situation is that $J_{\text{kex}} > J^H$ for any distance R and this is the reason for the spin-singlet configuration of H_2 in the ground state. In brief, electrons hopping (‘resonating’) between the sites, possible only in the total spin-singlet state $|\lambda_5\rangle$, contribute essentially to the bonding.

To verify the conceptual validity of the introduced Mott threshold for atomicity onset, we have plotted in figure 7 the Slater-orbital size α^{-1} as a function of R . Upon crossing the threshold R_{Mott} , α^{-1} indeed approaches rapidly with the further increasing R the $1s$ atomic size value $a_0 = 0.53 \text{ \AA}$. Instead, the main physical process contributing to the bonding are the virtual process between the sites. In effect, the ionicity and covalency factors lose their principal meaning for $R \gg 2.3 \text{ \AA}$.

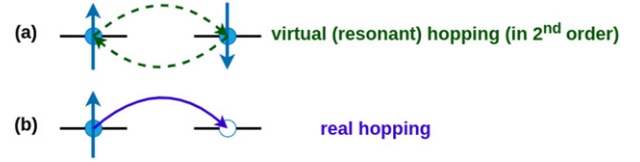


Figure 8. The virtual hopping processes that lead to the resonant covalency (a) and the real hopping, corresponding to the admixture of ionicity (b). For details see main text.

In conclusion, the dominant covalent character of H_2 molecule has a well defined meaning for $R \simeq R_{\text{bond}}$, as it is twice as large as the corresponding ionicity factor. However, this decomposition loses gradually its principal meaning as R increases and crosses beyond $R_{\text{Mott}} = 2.3a_0$. The ground state energy evolves slowly, but steadily toward, the atomic-limit value. Note also that the Hartree–Fock analysis (cf figure 2) provides unphysical results as this critical value of R is crossed. This means that, in the regime of large interatomic distance, the role of correlation becomes essential. In effect, our analysis is applicable then and can be systematically extended numerically by, e.g., enriching the single-particle basis. It would be also of general interest to ask if those concepts could be tested quantitatively by putting H_2 molecules on surfaces of other systems which would stretch the hydrogen-molecule size beyond the Mott–Hubbard threshold. Obviously, the analysis should then incorporate also the presence of the external surface potential of the substrate. However, this type of analysis goes beyond our goals here.

3.3. Physical reinterpretation of atomicity, covalency, and ionicity: resonant covalency

In order to provide a purely physical reinterpretation of covalency and ionicity we note that the form (3) of the covalent part contains sum of static products of the single-particle wave functions located on the sites 1 and 2 and their reverse; this is due to their indistinguishability in the quantum mechanical sense. On the contrary the coefficients γ_c and γ_i contain also virtual intersite processes depicted schematically in figure 8. In other words, the former factor contains a degree of atomicity in its static form, whereas the latter encompasses true dynamic virtual (hopping) processes of quantum-mechanical mixing. The question is how to separate those two factors into *atomicity* and *resonance covalency* parts in an analytic way.

To answer this dilemma we propose its following resolution. The allowed local (site) states are $|0, i\rangle$, $|\uparrow, i\rangle$, $|\downarrow, i\rangle$, and $|\downarrow, \uparrow, i\rangle$, i.e., the empty, single occupied with spin $\sigma = \uparrow$ or $\downarrow$, or the double atomic occupancies. Therefore, using the following identities

$$|0, i\rangle\langle 0, i| + \sum_{\sigma} |\sigma, i\rangle\langle \sigma, i| + |\uparrow, \downarrow, i\rangle\langle \uparrow, \downarrow, i| = \mathbb{I}, \quad (15)$$

and its equivalent second-quantized form involving site occupancies

$$\langle (1 - \hat{n}_{i\uparrow})(1 - \hat{n}_{i\downarrow}) \rangle + \langle \hat{n}_{i\uparrow}(1 - \hat{n}_{i\downarrow}) \rangle + \langle \hat{n}_{i\downarrow}(1 - \hat{n}_{i\uparrow}) \rangle + \langle \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \rangle = 1. \quad (16)$$

Noting that the probability of empty atomic configuration is equal to that doubly occupied, i.e., physically corresponding to the electron–hole symmetry in condensed-matter systems, we obtain the formula for single-electron occupancy in the final form [22]

$$\nu \equiv \sum_{\sigma} \langle \hat{n}_{i\sigma}(1 - \hat{n}_{i\bar{\sigma}}) \rangle = 1 - 2d^2. \quad (17)$$

Explicitly, we propose to decompose single-occupancy probability ν in the following manner

$$\nu \equiv a + c = 1 - 2d^2, \quad (18)$$

where a is the atomicity, and c is called the *resonant (true) covalency*, and $d^2 \equiv \langle \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \rangle$ denotes atom double occupancy probability. Now, the resonant covalency describes the degree of mixing due to the virtual hopping admixture to the frozen (atomic) configuration (cf figure 8(a)). In the strong-correlation limit ($r > 1$), it can be defined as $c \equiv [t + V]/(U - K)^2$ and expresses the contribution of the processes (a) to the two-particle wave function in the second order [23, 24] as expressed by ratio of virtual (double hopping, forth and back) process to the Coulomb interaction change in the intermediate step. Therefore, the atomicity is evaluated as

$$a = \nu - c = 1 - 2d^2 - c. \quad (19)$$

In the equilibrium state of H_2 , the resonant covalency reads $c \simeq 0.8$, whereas atomicity $a \simeq 0.1$ is practically negligible. Conversely, with increasing R , c decreases quite rapidly and approaches zero, whereas $a \rightarrow 1$, as anticipated.

Finally, in figure 9 we provide another characteristic containing atomicity, namely the R dependence d^2 . This double occupancy probability can also characterize the ionicity. The last formula shows that the atomicity is complete when $d^2 = 0$ and then $\nu = a = 1$ (i.e., for $R \gg R_{\text{Mott}}$). In the other words, the customarily, defined by (13) covalency, associated with the wave function (3), contains both atomicity and true covalency. For $R \gg R_{\text{Mott}}$ it involves mainly atomicity with a small admixture of c and d^2 . In this manner, the unphysical increase of γ_c with increasing R is resolved. In brief, fundamentally, we define the resonant (true) covalency c as proportional to the inverse Mottness, i.e.,

$$\text{true covalency} = 1/\text{Mottness} \quad \text{or} \quad c \equiv 1/4r. \quad (20)$$

In conclusion, based on our analysis of H_2 molecule we suggest that the covalency definition through the values of γ_c is not conceptually precise, whereas the ionicity is properly accounted for either by γ_i or $2d^2$. Additionally, in this way the *redefined covalency* is complementary to the *Mottness* and vice versa.

3.4. LiH and HeH^+ cases

We now apply the concepts introduced above for H_2 molecule to the cases of LiH and HeH^+ . In figures 10 and 11 we display the binding energies versus interatomic distance for HeH^+ molecular ion and LiH molecule, respectively. In the former case, the two $1s$ electrons are regarded as core electrons.

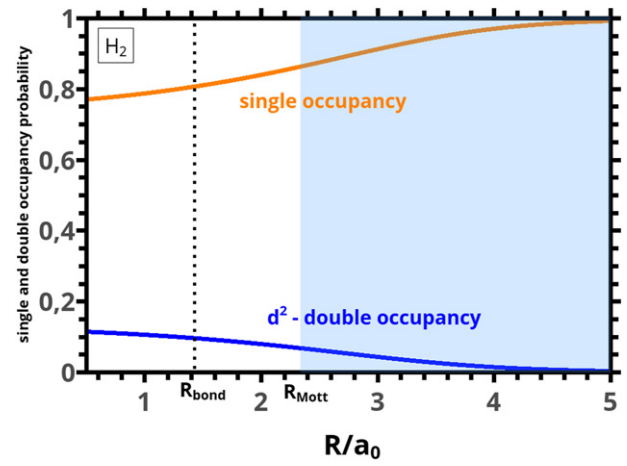


Figure 9. The atom double occupancy probability $d^2 \equiv \langle \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \rangle$ and simple occupancy ν , both vs R/a_0 , calculated for H_2 molecule using EDABI approach. Note the presence of inflexion point at $R = R_{\text{Mott}}$, signaling the onset of gradually increasing single occupancy (the orange curve). The single occupancy ν contains both resonant covalency and atomicity, which cannot be separated from each other at this stage. For detailed discussion see main text.

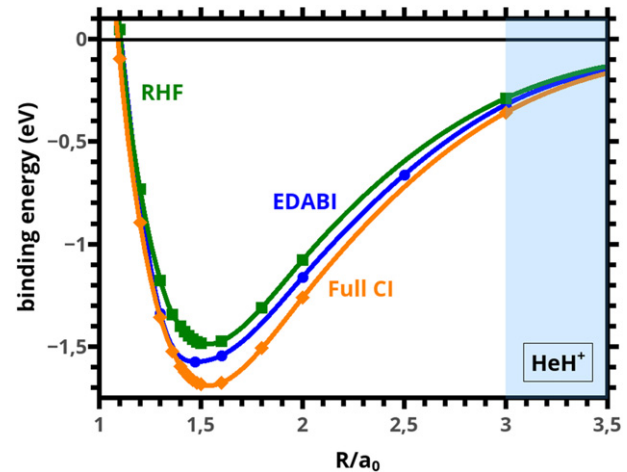


Figure 10. The HeH^+ binding energy versus relative interatomic distance, obtained using EDABI method and compared with RHF and full CI approach. a_0 is the Bohr radius.

Effectively, LiH is regarded as a molecule composed of one $2s$ electron due to Li and $1s$ electron due to H, with their orbitals adjustable when the interactions are included. Qualitatively, the character of these curves is similar to those of H_2 , depicted in figure 2. The quantitative factors are different though and, in particular, the bond length is slightly larger than that in H_2 case.

To characterize further those two cases we have plotted in figures 12 and 13 the covalency and ionicity factors for those two systems, respectively. Note that for LiH the ionicity is predominant in a wide range of R , whereas the opposite is true for HeH^+ . The difference arises from the circumstance that in LiH case the orbital size of $2s$ electron is decisively larger and has a higher energy leading to predominantly ionic configuration $\sim \text{Li}^{+0.9}\text{H}^{-0.9}$. In HeH^+ , molecular ion the bonding is largely

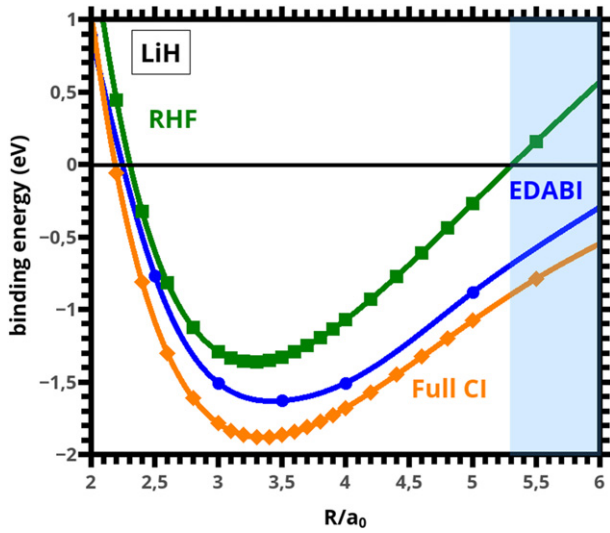


Figure 11. The LiH binding energy versus relative interatomic distance, obtained using EDABI method and compared with RHF and full CI approach. a_0 is the Bohr radius.

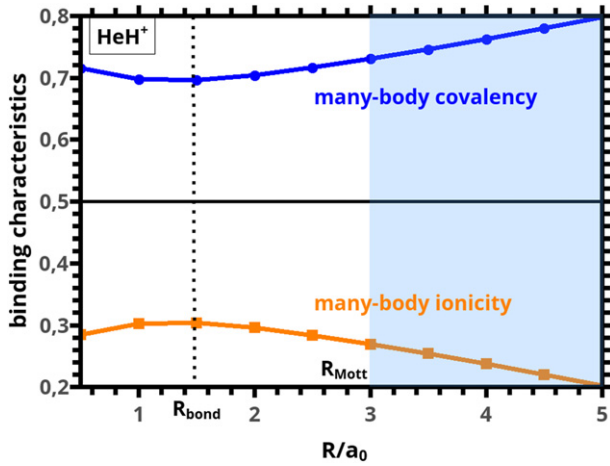


Figure 12. Many-body covalency vs many-body ionicity for HeH^+ molecule. The behavior is quite similar to that for H_2 molecule (cf figure 3).

covalent due to the fact that both two $1s^2$ He electrons hop (mix) with the H^+ state with no electrons in the corresponding $1s$ state.

One specific feature of those two systems should be noted, which is illustrated in figures 14 and 15, where the optimized sizes of the relevant orbitals has been shown. Namely, the size of $1s$ orbital of the He and $2s$ orbital of Li are strongly renormalized, the former largely expanded, whereas the latter contracted. The principal cause of this effect is the electronic correlation induced by the strong intraatomic (Hubbard) interaction $\sim U$. As this interaction in He is reduced by the flow of electron to the H^+ site, it is not so in the case of Li, where presence of the hydrogen electron strongly enhances the role of the interaction. In spite of those differences, both systems exhibit similar span of covalency regime. On the contrary, the incipient Mottness appears for larger distance R_{Mott} and this is presumably due to a larger renormalized-orbital

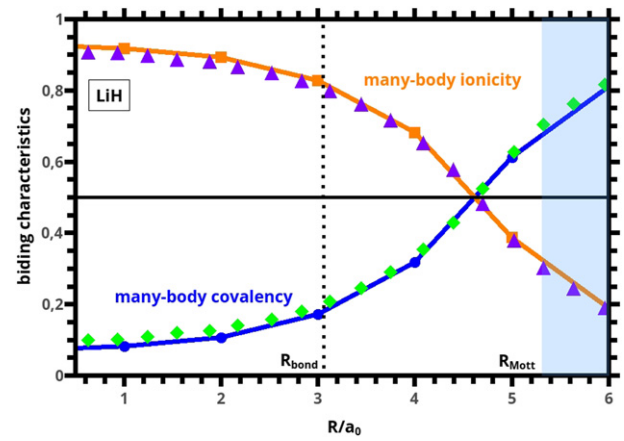


Figure 13. Many-body covalency vs many-body ionicity for LiH molecule. The points are taken from [19] for comparison. The covalency shows the same type of the unphysical R -dependence as in the case of H_2 .

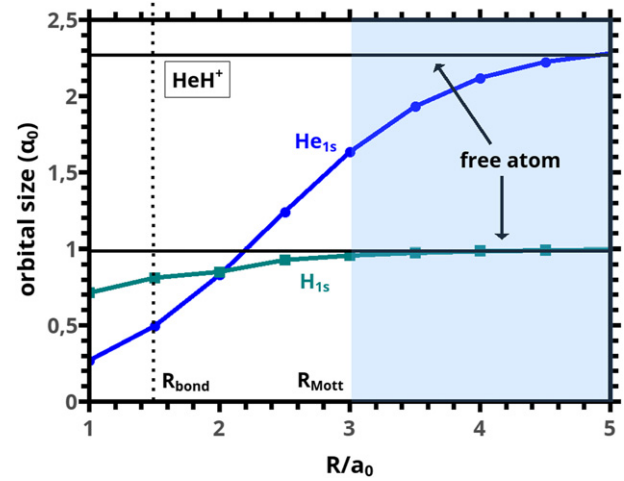


Figure 14. Atomic orbital size for He $1s$ and H $1s$ orbitals in HeH^+ molecular ion. Note that the Mott-type boundary has been drawn for the $1s$ states of He as this reached first upon increasing R .

size for Li. As can be seen from literature [25] and from our results here, HeH^+ is largely covalent and the whole analysis of a and c factors can be repeated here without any qualitative difference.

In table 1 we display the binding energies of the molecules H_2 , HeH^+ , LiH, regarded here as testing ground of our approach. For that reason we compare the obtained results with those deducted from other methods and with use of a richer single-particle basis. Even though our results are quantitatively not too accurate, they are obtained with simplest nontrivial basis, i.e., $1s$ states only for H_2 and HeH^+ cases, and with addition of $2s$ states on Li the LiH case. The EDABI results can be improved in a straightforward manner at the expense of computational resources. However in such a situation our following next discussion of bonding would be purely numerical. In other words, we accept the lower accurateness of E_G value within our method to allow for the analytic character of the subsequent discussion. One

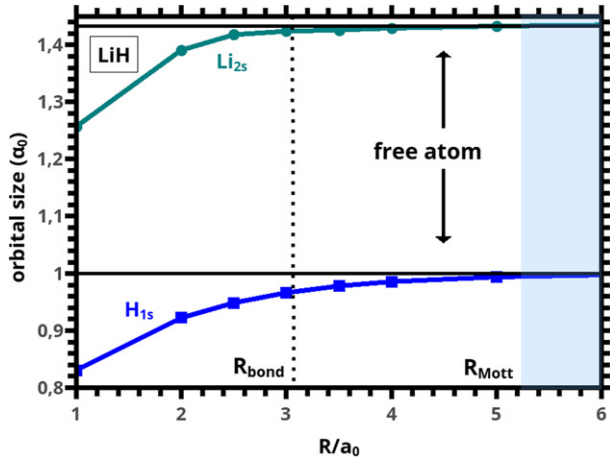


Figure 15. Atomic orbital size for H $1s$ and Li $2s$ orbitals in LiH molecule. Note the strong renormalization of atomic-orbital sizes, as well as a rapid convergence to the atomic values above $R = R_{\text{bond}}$, the latter being for the ionic bonding.

Table 1. Binding energy for H_2 , HeH^+ , and LiH molecules (in eV).

Method	H_2	HeH^+	LiH
EDABI	-4.0749	-1.5803	-1.6537
Full CI	-4.3824	-1.6849	-1.8846
RHF	-3.5963	-1.4839	-1.3616
Reference values	-4.3821[26]	-2.0542[27]	-1.3606[28]

can find more accurate value of ground state energy for HeH^+ [29].

4. Overall properties

We now compare results for those three model systems qualitatively. First, in figure 16 we plot relative contributions of the covalency and ionicity factors for the two-particle ground state (left), as well as a schematic size of the molecular orbitals relative to their original (atomic) size (right). The atomicity factor is not quantified at this stage. In the first two of them, the dynamics is solely due to $1s$ electrons, whereas in the LiH case the $1s^2$ configuration of electrons is frozen on Li and the whole dynamics is due to $1s-2s$ H-Li mixing and the corresponding interactions. This is the reason why LiH is largely ionic, whereas the remaining two are predominantly covalent, as illustrated in figure 13. One sees that the covalency in HeH^+ is larger than that for H_2 molecule, a rather unexpected intuitively result.

A separate discussion should be concerned with other overall properties of the systems studied. In table 2 the Mott (or Mott-Hubbard) critical distance R_{Mott} (in the units of a_0) is provided. This distance should be compared with the bond length R_{bond} calculated (cf table 3) according to three independent methods: EDABI, full CI, and RHF methods, respectively. We see that in each case R_{bond} is decisively lower than R_{Mott} . This means that the Mott-type boundary can be crossed only in the situation when the molecules are further apart, i.e., obtained artificially when, e.g., they are placed on surfaces

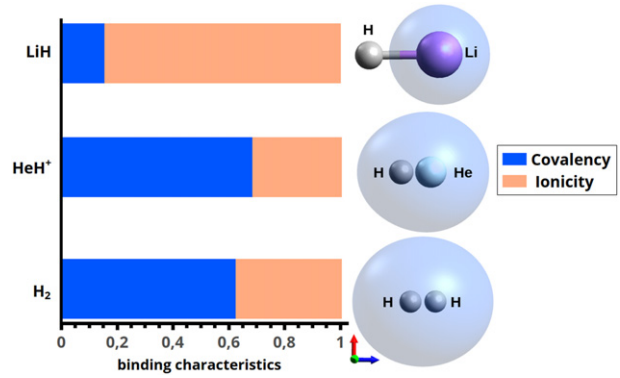


Figure 16. Schematic representation of the molecular orbitals for (isosurface probability density cut = 0.02) on the right, expressing relative covalency and ionicity contributions on the left.

Table 2. The interatomic distance corresponding to the Mott boundary regime calculated for H_2 , HeH^+ , and LiH molecules.

System	Mott boundary (a_0)
H_2	2.3
HeH^+	3.0
LiH	5.3

Table 3. Bond length for H_2 , HeH^+ , and LiH molecules (in units of a_0).>

Method	H_2	HeH^+	LiH
EDABI	1.430	1.469	3.382
Full CI	1.501	1.497	3.298
RHF	1.450	1.493	3.208
Reference values	1.398 [26]	1.463 [27]	3.015 [28]

with an external force elongating them. Particularly favorable situation occurs when molecules are placed in the environment with a large dielectric constant, as then interaction weakens and the bond length increases. Clearly, then the whole analysis must be revised and a realistic configuration with inclusion of appropriate external (surface) potential. We believe that the essential features of our analysis should survive when the molecule is placed in such environment, i.e., in a potential stretching equally both atoms.

In table 1 the binding energies are listed and compared with those from other methods. These numerical results present probably the weakest point of our EDABI method, since the corresponding values obtained are not very accurate. Nevertheless, we do not consider our method as a practical computing tool. Instead our main aim here was to extend, albeit at best in a semiquantitative manner, the basis for multi-electron covalency and ionicity, enriched by the concept of atomicity, all induced by the electronic correlations. Obviously, the approach can be extended in a straightforward manner by enlarging the single-particle basis and applied for the systems with larger atoms. Both of these factors have been considered by us before [7, 9] for model systems, with one limitation, that we have not analyzed there the bonding properties. This

Table 4. Calculated EDABI values of the equilibrium parameters for LiH, HeH⁺, and H₂ molecules.

Parameter	LiH	H ₂	HeH ⁺
E_G (eV)	−217.45	−31.198	−79.675
U_{1sLi} (eV)	49.062	N/A	N/A
U_{1sH} (eV)	18.559	22.490	19.592
U_{1sHe} (eV)	N/A	N/A	14.925
U_{2sLi} (eV)	12.784	N/A	N/A
t (eV)	−21.150	−9.9049	−15.674
K (eV)	14.368	13.007	11.374
α_{1sH} (a_0^{-1})	1.035	1.194	1.240
α_{1sHe} (a_0^{-1})	N/A	N/A	2.095
α_{2sLi} (a_0^{-1})	1.329	N/A	N/A

analysis should be explored further along the lines discussed here.

Finally, in table 4 we list the most important microscopic parameters in the equilibrium state. A more detailed analysis of those is presented in appendix B. The values of Coulomb-interaction parameters will be reduced by the dielectric constant factor if system under consideration is placed on surface of an insulating material. This should rescale all the parameter values accordingly.

5. Outlook

The reason for selecting the three systems analyzed here is caused by the circumstance that HeH⁺ is strongly covalent, LiH strongly ionic, and H₂ can be placed in between them. On example of the last of them our novel concept of atomicity and resonant covalency have been proposed.

The introduced here atomicity for the case of molecular system (corresponding to Mott–Hubbard localization effects in periodic systems) amounts to specifying a gradual transformation from molecular to atomic language in describing their electronic states, as a function of interatomic distance. This changeover is the basic feature and is associated with the essential change in regarding those particles as evolving within *indistinguishable* (molecular) character and acquiring eventually the form of *distinguishable* (atomic) states.

One must also underline that the concept of atomicity here is quantitative in nature. This is because the Mott–Hubbard localization concept in condensed-matter systems [13, 20] appears usually as a first-order transition, requiring the energy equality of the two macro configuration (delocalized, localized) at this phase transition. Here the evolution may be regarded as a supercritical behavior at best [13, 30, 31]. However, the antiferromagnetic kinetic exchange survives even when the states are becoming orbitally distinguishable [32].

Certainly, a further insight is required to quantify the present discussion for more complex systems. The present concepts are proposed to clarify the obviously *unphysical behavior* of the increasing covalency with the increasing interatomic distance. As far as we are aware of, this inconsistency, although intuitively understandable, has not been discussed

explicitly in the quantum-chemical literature. Also, the emerging atomicity here squares well with the Mott’s original argument [20] that the metallic (covalent) state of electrons in a periodic system is ruled out at (semi)macroscopic interatomic distances.

Acknowledgments

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Appendix A. Eigenvalues and eigenstates for H₂ molecule

Starting from the orthogonalized restricted basis, we define the field operators as

$$\hat{\psi}_\sigma(\mathbf{r}) = w_1(\mathbf{r})\chi_\sigma(1)\hat{a}_{1\sigma} + w_2(\mathbf{r})\chi_\sigma(2)\hat{a}_{2\sigma}, \quad (\text{A.1})$$

$$\hat{\psi}_\sigma^\dagger(\mathbf{r}) = w_1^*(\mathbf{r})\chi_\sigma(1)\hat{a}_{1\sigma}^\dagger + w_2^*(\mathbf{r})\chi_\sigma(2)\hat{a}_{2\sigma}^\dagger, \quad (\text{A.2})$$

or, in compact notation, as

$$\hat{\psi}(\mathbf{r}) \equiv \begin{pmatrix} \hat{\psi}_\uparrow(\mathbf{r}) \\ \hat{\psi}_\downarrow(\mathbf{r}) \end{pmatrix}. \quad (\text{A.3})$$

In the above, $\hat{a}_{i\sigma}$ and $\hat{a}_{i\sigma}^\dagger$ are electron annihilation and creation operators in the state $w_{i\sigma}(\mathbf{r}) \equiv w_i(\mathbf{r})\chi_\sigma(i)$. Also, as we restrict here to *s*-orbital systems, the molecular (Wannier) functions can be taken as real if the condition $J' = J^H$ holds. Using the representation (A.3), we obtain Hamiltonian (1) with the microscopic parameters expressed through the Slater orbitals and coefficients β and γ (cf equation (5)), or explicitly through inverse orbital size α and interatomic distance R (see e.g. [7, 9]). The relevant physical quantities may be thus obtained as a function of R , with the orbital parameter α optimized in each case.

To obtain the ground state energy E_G for fixed R , the Hamiltonian (1) is diagonalized. This is carried out by making use of the global symmetry respecting two-particle states, leading to block-diagonal many-body Hilbert space, with specified values of the total spin, S , and its *z*-component, S^z , as well with transposition antisymmetry preserved. In effect, one can start

Table B1. Ground state energy and microscopic parameters for H₂ molecule (in eV).

$R (a_0)$	E_G/N	ϵ	t	U	K	J	V
0.5	-657	-14.29	-31.75	30.06	19.43	0.43	-0.28
1	-1486	-22.51	-15.95	25.29	15.43	0.36	-0.19
1.5	-1558	-23.84	-9.21	22.08	12.67	0.29	-0.16
2	-1516	-23.41	-5.79	19.96	10.75	0.23	-0.16
2.5	-1461	-22.56	-3.84	18.61	9.34	0.18	-0.16
3	-1418	-21.67	-2.62	17.81	8.24	0.13	-0.16
3.5	-1389	-20.86	-1.82	17.38	7.35	0.09	-0.16
4	-1373	-20.15	-1.26	17.18	6.60	0.06	-0.15
4.5	-1365	-19.52	-0.86	17.09	5.95	0.04	-0.14
5	-1362	-18.98	-0.59	17.05	5.40	0.02	-0.12

the basis of $\binom{4}{2} = 6$ following states

$$\left\{ \begin{array}{l} |1\rangle = \hat{a}_{1\uparrow}^\dagger \hat{a}_{2\uparrow}^\dagger |0\rangle, \\ |2\rangle = \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\downarrow}^\dagger |0\rangle, \\ |3\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle, \\ |4\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger - \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle, \\ |5\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger + \hat{a}_{2\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle, \\ |6\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger - \hat{a}_{2\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger) |0\rangle. \end{array} \right. \quad (\text{A.4})$$

The first three are the spin-triplet states with $S^z = +1, -1, 0$, whereas the next three are inter- and intra-site singlets, respectively. The triplet state does not hybridize with other states and provides three 1×1 irreducible blocks with eigenvalues $\lambda_1 = \lambda_2 = \lambda_3 = \epsilon_1 + \epsilon_2 + K - J^H$. The remaining three singlet states compose the 3×3 block, so the Hamiltonian in that Fock subspace takes the form

$$\hat{\mathcal{H}} = \begin{pmatrix} \epsilon + K + J^H & 2(t + V) & 0 \\ 2(t + V) & 2\epsilon + J + U & \frac{1}{2}(U_1 - U_2) \\ 0 & \frac{1}{2}(U_1 - U_2) & 2\epsilon + U - J^H \end{pmatrix}, \quad (\text{A.5})$$

where $\epsilon \equiv (\epsilon_1 + \epsilon_2)/2$ and $U \equiv (U_1 + U_2)/2$. This formulation allows to apply this formalism to both H₂ (where $U_1 = U_2 = U$ and $\epsilon_1 + \epsilon_2 = \epsilon$), and to HeH⁺ and LiH, where those simplifications are not met due to inequivalent atoms involved.

In the case of H₂, the eigenvalues of equation (A.5) take the form

$$\lambda_{4,5} = 2\epsilon + \frac{1}{2}(K + U) + J \pm \frac{1}{2}D, \quad (\text{A.6})$$

$$\lambda_6 = 2\epsilon + U - J, \quad (\text{A.7})$$

with $D \equiv [(U - K)^2 + 16(t + V)^2]^{\frac{1}{2}}$. The corresponding eigenstates are

$$|\lambda_{4,5}\rangle \equiv |\lambda_{\pm}\rangle = \frac{1}{[D(D \pm U \mp K)]^{\frac{1}{2}}} [(4(t + V))|4\rangle \pm (D \pm U \mp K)|5\rangle], \quad (\text{A.8})$$

where, for simplicity, we have defined the atomic-limit energy as the reference point, $\epsilon = 0$. We note that the eigenstates $|\lambda_{4,5}\rangle$ are superposed of the symmetric ionic state $|5\rangle$ and covalent part $|4\rangle$. The state $|\lambda_5\rangle$ is the ground state as the λ_5 eigenvalue is the lowest one. In the limit $U \gg |t + V|$, the λ_5 eigenvalue reads

$$\lambda_5 \simeq 2\epsilon + J^H + K - \frac{4(t + V)^2}{U - K}. \quad (\text{A.9})$$

The last term on the right-hand side of equation (A.9) is the so-called kinetic-exchange contribution. It competes with ferromagnetic Heisenberg exchange $\sim J^H$. In similar manner, the two-particle states for HeH⁺ and LiH are obtained, except that in those two cases, the diagonalization of the Hamiltonian matrix (A.5) cannot be carried out analytically, since the $\epsilon_1 \neq \epsilon_2$ and $U_1 \neq U_2$. The singlet state $|\lambda_5\rangle$ is elaborated further throughout the main text.

Appendix B. Tables of relevant quantities and parameters for considered systems

In tables B1–B3 we provide relevant quantities and microscopic parameters versus R , obtained within EDABI scheme for the three systems discussed in main text, i.e., H₂, HeH⁺, and LiH.

Note that the value of $|t|$ is comparable to U in the limit $R < R_{\text{bond}}$ and diminishes spectacularly when $R > R_{\text{bond}}$ (i.e. in the strong-correlation regime).

The RHF and CI computations were carried out using the GAMESS code and the 6–31 G basis set to represent the Slater functions. Numerical accuracy for the EDABI calculations is $10^{-4} a_0$ for R and 10^{-5} eV for energy, respectively.

Table B2. Ground state energy and microscopic parameters for HeH⁺ molecular ion (in eV).

$R(a_0)$	E_G/N	ϵ_H	ϵ_{He}	t	U_H	U_{He}	K	V
0.5	−27.84	−22.42	−14.32	−24.07	22.35	36.70	11.17	−0.99
1	−38.54	−32.81	−32.43	−18.96	20.57	21.85	8.48	−0.75
1.5	−39.84	−34.59	−33.13	−15.49	19.54	14.62	6.72	−0.60
2	−39.63	−34.10	−29.57	−13.15	18.95	11.10	5.66	−0.50
2.5	−39.38	−32.20	−25.93	−11.55	18.61	9.39	4.95	−0.44
3	−39.21	−29.67	−22.86	−10.38	18.41	8.56	4.54	−0.39
3.5	−37.68	−27.20	−20.45	−9.45	18.30	8.15	4.26	−0.36
4	−39.09	−25.08	−18.62	−8.64	18.23	7.96	4.05	−0.33
4.5	−38.97	−23.37	−17.23	−7.90	18.19	7.86	3.86	−0.31
5	−38.92	−22.01	−16.16	−7.20	18.17	7.82	3.69	−0.31

Table B3. Ground state energy and microscopic parameters for LiH molecule (in eV).

$R(a_0)$	E_G/N	ϵ_H	ϵ_{2sLi}	t	U_H	U_{2sLi}	K	V
1	−98.21	−43.25	−39.32	−55.89	38.29	33.08	21.19	−1.70
1.5	−105.89	−44.47	−40.24	−48.02	35.13	26.34	19.79	−1.52
2	−108.10	−45.402	−40.97	−37.97	32.02	22.01	17.10	−1.02
2.5	−108.88	−45.73	−41.97	−30.93	28.89	17.98	16.77	−0.89
3	−109.29	−46.12	−42.53	−24.43	24.80	14.04	15.12	−0.78
3.5	−109.35	−45.93	−41.55	−19.89	22.08	11.35	13.29	−0.69
4	−109.29	−45.81	−41.53	−14.05	20.30	9.44	11.98	−0.51
4.5	−109.04	−45.50	−41.44	−11.23	19.19	8.41	10.13	−0.38
5	−108.92	−45.75	−41.39	−8.09	18.09	7.75	9.48	−0.32
5.5	−108.71	−44.96	−40.91	−5.48	18.25	7.48	6.32	−0.28
6	−108.32	−44.49	−40.76	−4.01	17.98	7.25	4.01	−0.26

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Toward Complementary Characterization of the Chemical Bond

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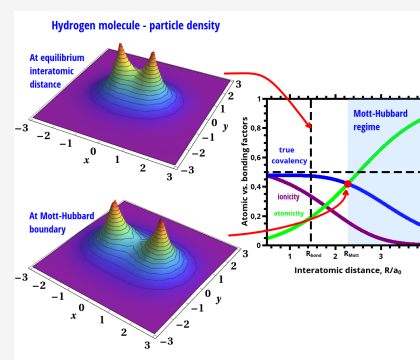


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Supporting Information

ABSTRACT: A precise discussion of a single bond requires consideration of two-particle wave function for the particles involved. Here we define and determine rigorously the intrinsic covalency and connected characteristics of the canonical example of the H_2 molecule. This is achieved by starting from an analytic form for the two-particle wave function for electrons forming the bond, in which we single out the atomic contribution (*atomicity*) in an unequivocal manner. The presence of the *atomicity* and ionicity factors complements the existing attributes of the bond. In this way, a gradual evolution of the molecular state to its two-atom correspondent is traced systematically with increasing interatomic distance. In effect, a direct relation to the onset of incipient Mott-Hubbard atomicity (*Mottness*) to the intrinsic covalency and ionicity is established. This goal is achieved formally by combining the single-particle wave function readjustment in the entangled state with a simultaneous determination of two-particle states in the particle (second quantization) representation.



The concept of a chemical bond and its quantum properties is of fundamental importance to our understanding of both physical and chemical characteristics of molecules and solid-state compounds.^{1–3} Among the principal questions are those of the relative roles of covalency, ionicity, and atomicity, as they describe qualitative differences with the characteristics of parent atomic states composing the system. Historically, the chemical bond was described in a quantitative manner by Heitler and London⁴ (see also Condon⁵)—who introduced the two-particle wave function in the Hartree–Fock approximation that is composed of atomic wave functions of electrons centered on atoms. This inconsistency in an otherwise pioneering approach needed refinement to include a quantum-mechanical mixing of the atomic orbitals.^{6–8} In effect, the approach is a complete single-particle formulation of the intrinsic many-particle problem.

Here we propose a resolution of the question concerning the evolution of the molecular states into the corresponding atomic configuration within the many-particle picture. Such an approach leads to an unequivocal determination of *true covalency*, incorporating a novel concept of *atomicity*, in addition to the *ionicity*. In this way, we resolve the longstanding fundamental question of unphysical behavior of covalency with the increasing interatomic distance as well as observe a gradual evolution of the correlated molecular Hund–Mulliken (Hückel–Slater) orbitals into their Heitler–London atomic correspondents with the increasing interatomic distance, $R \rightarrow \infty$.

At the outset, we take a multiparticle view of the chemical bond and implement a special method EDABI (Exact Diagonalization **A**b Initio approach) devised in our group earlier^{9–11} and apply it here to a rigorous analysis in the

simplest situation of the H_2 molecule. The generic case of the H_2 molecule involves a two-electron single bond, and thus the role of interelectronic correlations in combination with concomitant molecular single-particle wave-function readjustment in the resultant (correlated) state can be analyzed rigorously and in mathematically analytic terms.

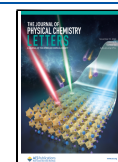
Our formulation differs essentially from the discussion concerning, among others, the role of electron correlations in the chemical bonding,^{12–19} as neither the *atomicity* nor *intrinsic covalency* factors are singled out or even discussed explicitly. The introduction of *atomicity* is indispensable to obtain correct bonding characteristics behavior, as discussed in detail below. In this sense, we introduce a complementary description in the quantum-mechanical language, as it contains both “delocalized” (molecular) and “localized” (atomic) ingredients to complete the picture.

The structure of this Letter is as follows. After introducing an exact two-particle electron wave function, we redefine the covalency to extract from the standard definition the contribution of atomicity, by referring to the notions of Mott and Hubbard localization. This new formulation allows us to define and determine explicitly the true covalency, atomicity (also termed seniority²⁰), and ionicity factors in the chemical bond and hence to understand those component factors of the chemical bond in a fully quantitative manner. The whole

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methodology is based on a combination of both the first- and second-quantization aspects of the relevant multielectron states, detailed in the [Supporting Information](#).

By applying the procedure outlined in the Method and in [Supporting Information](#) we obtain a two-particle wave function in an explicit form

$$\begin{aligned}\Psi_0(\mathbf{r}_1, \mathbf{r}_2) &= \frac{2(t+V)}{\sqrt{2D(D-U+K)}} \Psi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad - \frac{1}{2} \sqrt{\frac{D-U+K}{2D}} \Psi_{\text{ion}}(\mathbf{r}_1, \mathbf{r}_2) \equiv \\ &\equiv C\Psi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) + I\Psi_{\text{ion}}(\mathbf{r}_1, \mathbf{r}_2)\end{aligned}\quad (1)$$

where the covalent (Ψ_{cov}) and ionic (Ψ_{ion}) parts are, respectively

$$\begin{aligned}\Psi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) &= [w_1(\mathbf{r}_1)w_2(\mathbf{r}_2) + w_1(\mathbf{r}_2)w_2(\mathbf{r}_1)] \\ &\quad \times [\chi_\uparrow(\mathbf{r}_1)\chi_\downarrow(\mathbf{r}_2) - \chi_\downarrow(\mathbf{r}_1)\chi_\uparrow(\mathbf{r}_2)]\end{aligned}\quad (2)$$

$$\begin{aligned}\Psi_{\text{ion}}(\mathbf{r}_1, \mathbf{r}_2) &= [w_1(\mathbf{r}_1)w_1(\mathbf{r}_2) + w_2(\mathbf{r}_1)w_2(\mathbf{r}_2)] \\ &\quad \times [\chi_\uparrow(\mathbf{r}_1)\chi_\downarrow(\mathbf{r}_2) - \chi_\downarrow(\mathbf{r}_1)\chi_\uparrow(\mathbf{r}_2)]\end{aligned}\quad (3)$$

where $\{w_i(\mathbf{r})\}_{i=1,2}$ are trial Hückel-Slater molecular orbitals and $\{\chi_\sigma(i)\}_{\sigma=\pm 1}$ are spin functions. In the above expression the microscopic parameters U and K are the magnitudes of intra-atomic and interatomic Coulomb repulsion, respectively, t and V are the magnitudes of hopping (Bloch integral) and so-called correlated hopping, respectively (for details see Methods), and

$$D \equiv \sqrt{(U-K)^2 + 16(t+V)^2} \quad (4)$$

We note that the two-particle wave function has the Heitler–London form, except the coefficients contain **all** interparticle interaction terms, and the single-particle wave functions are the molecular Hückel-Slater orbitals with their adjusted size in the resultant correlated state. This two-particle wave function may be rewritten in terms of the original Slater orbitals as follows

$$\begin{aligned}\Psi_0(\mathbf{r}_1, \mathbf{r}_2) &= (C\beta^2(1+\gamma^2) - 2\gamma I\beta^2)\phi_{\text{cov}}^{\text{at}}(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad + (I\beta^2(1-\gamma^2) - 2\gamma C\beta^2)\phi_{\text{ion}}^{\text{at}}(\mathbf{r}_1, \mathbf{r}_2) \\ &\equiv \tilde{C}\phi_{\text{cov}}^{\text{at}} + \tilde{I}\phi_{\text{ion}}^{\text{at}}\end{aligned}\quad (5)$$

where the coefficients β and γ are defined through the relation

$$w_{i\sigma}(\mathbf{r}) = \beta[\psi_{i\sigma}(\mathbf{r}) - \gamma\psi_{j\sigma}(\mathbf{r})] \quad (6)$$

where i and j label the atoms, and $\sigma \equiv \pm 1 \equiv \uparrow, \downarrow$ is the electron spin quantum number. Note that $\langle w_i(\mathbf{r})|w_j(\mathbf{r}) \rangle = \delta_{ij}$, β , and γ are the mixing coefficients of the neighboring Slater orbitals ($\psi_{i\sigma} \equiv \psi(\mathbf{r} - \mathbf{R}_i)\chi_\sigma(i) \equiv (\sqrt{\alpha^3/\pi}) \times \exp(-\alpha|\mathbf{r} - \mathbf{R}_i|)\chi_\sigma(i)$, (in which α^{-1} is the size of the orbital). The functions $\phi_{\text{cov}}^{\text{at}}(\mathbf{r}_1, \mathbf{r}_2)$ and $\phi_{\text{ion}}^{\text{at}}(\mathbf{r}_1, \mathbf{r}_2)$ have the same form as (2) and (3), respectively, except for the replacement $w_{i\sigma}(\mathbf{r}) \rightarrow \psi_{i\sigma}(\mathbf{r})$.

We define the effective atomic contribution $\tilde{A}$ at given interatomic distance R as

$$\lim_{\gamma \rightarrow 0} \tilde{C} = C\beta^2 \equiv \tilde{A} \quad (7)$$

that is, we regard it as the weight of the atomic part at the same R . Formally, the true covalency, ionicity, and atomicity are then defined for a given R as

$$\text{covalency: } \gamma_{\text{cov}} \equiv \frac{|\tilde{C}|^2 - |\tilde{A}|^2}{|\tilde{C}|^2 + |\tilde{I}|^2} \quad (8)$$

$$\text{ionicity: } \gamma_{\text{ion}} \equiv \frac{|\tilde{I}|^2}{|\tilde{C}|^2 + |\tilde{I}|^2} \quad (9)$$

$$\text{atomicity: } \gamma_{\text{at}} \equiv \frac{|\tilde{A}|^2}{|\tilde{C}|^2 + |\tilde{I}|^2} \quad (10)$$

The original motivation for introducing the concept of atomicity is as follows: It may seem natural to define covalency as $|\tilde{C}|^2/(|\tilde{C}|^2 + |\tilde{I}|^2)$ and ionicity as $|\tilde{I}|^2/(|\tilde{C}|^2 + |\tilde{I}|^2)$. However, such a choice leads directly to unphysical features (see [Supporting Information](#)). Namely, $|\tilde{C}|^2/(|\tilde{C}|^2 + |\tilde{I}|^2)$ reaches its maximal value of unity in the limit of separate atoms ($R \rightarrow \infty$). This is also the limit when electrons are entirely localized on their parent atoms and become distinguishable in the quantum-mechanical sense. This is the limit that we regard as that atomicity equal to unity and vanishing true covalency. This type of argument is also the reason for subtracting the probability $\tilde{A}^2$ from $\tilde{C}^2$, not the corresponding wave-function amplitudes. The quantities (8)–(10) are proved next to be useful and of crucial importance.

To demonstrate the fundamental meaning of the introduced quantities we relate them to the criteria of Mott²¹ and Hubbard²² for onsets of localized (atomic) behavior. This is because the evolution of molecular H_2 (electron-paired) state into individual separate singly occupied (atomic) states is regarded as equivalent to the Mott–Hubbard localization (for a recent related discussion in different context see, e.g., ref 23). Namely, we define Mott and Hubbard onset criteria as

$$\frac{2t+V}{U-K} = 1 \quad \text{and} \quad n_c^{1/d}\alpha^{-1} \equiv \frac{1}{\alpha_0 R_{\text{Mott}}} \simeq 0.5 \quad (11)$$

respectively, where α_0 is the readjusted inverse orbital size, here at $R = R_{\text{Mott}}$. The first of them implies that, for $R = R_{\text{Mott}}$ the kinetic (hopping) energy is equal to the correlation energy; that is, for $R < R_{\text{Mott}}$ the ratio is greater than unity, whereas for $R > R_{\text{Mott}}$ it is smaller than unity and reduces quite rapidly to zero with increasing R beyond R_{Mott} . In other words, the kinetic energy dominates in the former case and enhances hopping electrons to resonate strongly between the sites, whereas the electrons become gradually frozen as R increases beyond R_{Mott} . On the other hand, the Mott criterion expresses the onset of localization in terms of the renormalized single-particle wave function size at the localization threshold. Namely, the threshold is reached when the diameter of the orbital in the correlated state ($2\alpha_0^{-1}$) is equal to the interorbital distance ($R = R_{\text{Mott}}$). Semiclassically, it means that the collective character is established when the orbitals start overlapping.

To visualize this formal reasoning we have plotted in [Figure 1](#) the left parts of both (11) as a function of R as well as have marked by red points their values at R_{Mott} . The blue shaded area may be called the *Mottness regime*.²⁴ The inset shows the corresponding dependence of the renormalized size of the Slater orbital in the correlated state, with the dotted vertical line marking the equilibrium bond length $R_{\text{bond}} \simeq 1.43a_0$. Note

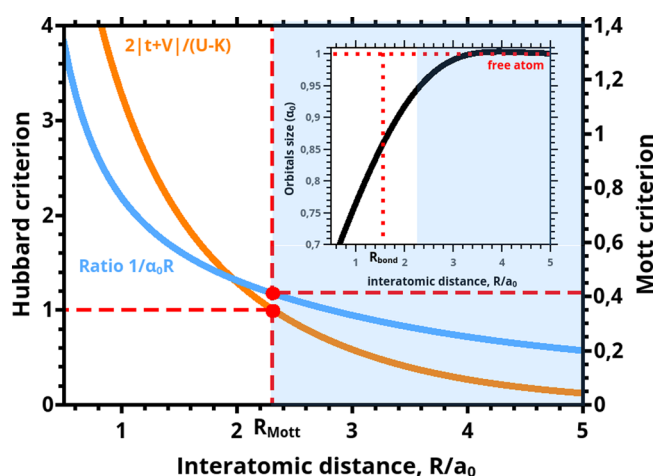


Figure 1. Hubbard (orange) and Mott (blue) characteristics of atomicity vs interatomic distance R (dashed horizontal lines). The dots mark the points corresponding to Hubbard and Mott criteria. The vertical dotted line marks the onset of Mottness at R_{Mott} . (inset) R dependence of the orbital size of the renormalized atomic wave functions composing the molecular (Wannier) single-particle states. The dotted line marks the equilibrium distance R_{bond} .

that the orbital size for $R > R_{\text{Mott}}$ approaches rapidly to the free-atom values a_0 .

The explicit connection of the above onset to the true covalency (γ_{cov}), ionicity (γ_{ion}), and atomicity (γ_{at}) is visualized in Figure 2, where the R dependence of those quantities is drawn. Remarkably, at the distance R_{Mott} the true covalency and atomicity acquire the same value, so the point R_{Mott} is a crossover point from true-covalency dominated to atomicity (Mottness) regime. Furthermore, γ_{cov} is predominant for $R < R_{\text{Mott}}$ whereas γ_{at} is for $R > R_{\text{Mott}}$ as it should. Additionally, the covalency and ionicity (atom double occupancy) coincide as R

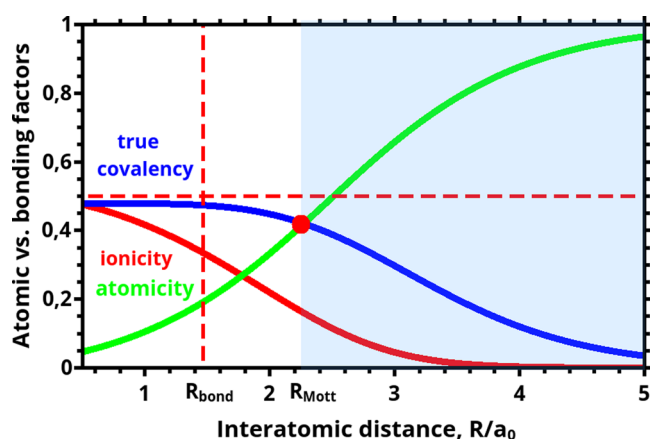


Figure 2. Intrinsic properties of the chemical bond: atomicity (green), true covalency (blue), and ionicity (red), all as a function of interatomic distance R . They represent the relative weights in the total two-particle wave function. In the $R \rightarrow 0$ limit the atomicity practically disappears and is the only contribution in the separate-atom limit $R \rightarrow \infty$. The solid circle defines the onset of localization effects (Mottness) due to interelectronic correlations. If the atomicity is disregarded, the covalency exhibits a drastic nonphysical behavior with increasing $R > R_{\text{bond}}$. The figure illustrates a systematic evolution of molecular states into separate atoms and, vice versa, the formation of molecular states out of separate atoms. The Slater states have a renormalized size $\alpha^{-1} \leq \alpha_B$.

$\rightarrow 0$, whereas then $\gamma_{\text{at}} \rightarrow 0$. Both γ_{cov} and γ_{ion} disappear in the atomic limit ($R \gg R_{\text{Mott}}$), where $\gamma_{\text{at}} \rightarrow 1$. The results presented in Figure 2 illustrate one of the central findings of the present work. The principal characteristics are detailed further in Tables 1 and 2. In Table 1 we list the discussed factors of

Table 1. Equivalent Characteristics of the Atomicity Onset Threshold^a

characteristic	value
Mott criterion	0.42
Hubbard criterion	1
covalent-atomic crossover	$2.285a_0$
R_{Mott}	$2.279a_0$

^aFor details see the main text.

Table 2. Particle Density at the Midpoint, Inverse Orbital Size α_0 , and Mixing Coefficients β and γ , all Versus R^a

$R (a_0)$	$n(0, 0)$	α_0	β	γ
1	0.334	1.307 51	1.1386	0.478 11
1.43	0.267	1.198 38	1.0854	0.388 77
2.3	0.142	1.054 28	1.0338	0.253 58
4	0.023	0.998 601	1.0012	0.048 640

^aThe particle density $n(0, 0)$ illustrates the gradually vanishing electron density in the region between the atoms as R increases beyond R_{Mott} .

Mottness onset to show that they are mutually consistent. This agreement leads to the conclusion that the introduced entities (8)–(10) are not only relevant for the description of the Mott–Hubbard localization in condensed-matter (extended) systems but also appear as a crucial incipient feature in molecular systems. We stress, this was possible only by introducing a two-particle wave function as the proper characteristic of a single bond, which, after all, is composed of electron pairs.

So far, our discussion was based on wave-function mechanics. In the remaining part we reformulate the analysis directly in the second-quantization language, which will allow us to provide the physical interpretation of the bond in terms of particle densities. Namely, to amplify our multiparticle bond description we return to the particle language and display in Figure 3 several panels composed of electron density in the (x, y) plane, with the protons distant by $R/a_0 = 1, 1.43 (R_{\text{bond}}), 2.3 (R_{\text{Mott}})$, and 4 (profiles a–d), respectively. The density is defined as

$$n_{\sigma}(\mathbf{r}) = \langle \psi_G | \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) | \psi_G \rangle \quad (12)$$

where $|\psi_G\rangle$ is the lowest spin-singlet eigenstate and $\hat{\psi}_{\sigma}(\mathbf{r})$ is the field operator. One should note that this density when integrated and summed over spin directions ($\sigma = \pm 1$) is equal to the total number of particles ($N_e = 2$). Obviously, $n_{\uparrow}(\mathbf{r}) = n_{\downarrow}(\mathbf{r}) \equiv n(\mathbf{r})/2$, where $n(\mathbf{r})$ is the total density. More importantly, this quantity provides the physical density, in contrast to the probability density $|\psi_G(\mathbf{r}_1, \mathbf{r}_2)|^2$. This distinctive feature of $n(\mathbf{r})$ shows that the density diminishes in the region between the atoms to zero relatively fast with the increasing R above R_{Mott} . To substantiate the last statement we have listed in Table 2 the density value $n(0, 0)$ in the middle point between the proton positions. For the sake of comparison, we have also added there the inverse orbital size as well as the mixing coefficients in the wave function $w_i(\mathbf{r}) = w(\mathbf{r} - \mathbf{R}_i)$ to

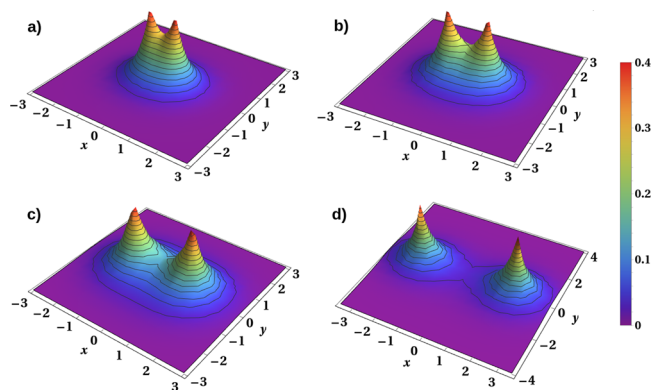


Figure 3. Electron density $n_e(\mathbf{r})$ for different interatomic distances. (a) $R = 1a_0^{-1}$, (b) $R = 1.43a_0^{-1}$, (c) $R = 2.3a_0^{-1}$, (d) $R = 4a_0^{-1}$. The parts centered at nuclei are practically disjoint for $R \geq 5a_0$, illustrating the robustness of atomic behavior in that situation. This density contains also the double-occupancy (ionicity) contribution, which becomes rapidly negligible with increasing R beyond R_{Mott} .

show that, indeed, both two- and single-particle characteristics merge into their atomic correspondents as R increases beyond R_{Mott} . Note that, whereas γ expresses the decreasing Pauling covalency,²⁵ $n(0, 0)$ describes the diminishing true covalency.

Analogously, we can define the concentration of the electrons in an ionic configuration as follows

$$n_{\text{ion}}(\mathbf{r}) \equiv \langle \psi_G | \hat{n}_\sigma(\mathbf{r}) \hat{n}_{\bar{\sigma}}(\mathbf{r}) | \psi_G \rangle \quad (13)$$

with $\hat{n}_\sigma(\mathbf{r}) \equiv \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r})$ and $\bar{\sigma} \equiv -\sigma$. In other words, $n_{\text{ion}}(\mathbf{r})$ expresses the density of local spin-singlet pairs (double-site occupancy). Profiles of $n_{\text{ion}}(\mathbf{r})$ are not presented explicitly, as they are contained in the equivalent form as the second part of the wave function (5).

Finally, along with the definitions (12) and (13) of local particle densities, we can define the nonlocal density of covalent electrons in the following manner.

$$n_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) = \langle \psi_G | \hat{n}_\sigma(\mathbf{r}_1) \hat{n}_{\bar{\sigma}}(\mathbf{r}_2) | \psi_G \rangle \quad (14)$$

This expression for a correlation function completes our description in both the first- and second-quantization schemes. The expressions (12)–(14) may be useful in the situations with more involved orbitals.

To recap, our analysis of a single chemical bond is based entirely on the multiparticle description, both in the first- and second-quantization schemes. Both of these descriptions are equivalent, but within the second part of them it is possible to relate it directly to the particle language. In general, the approach provides a precise revision of the bond factors as well as complements the current intense discussion^{12–19} of the correlation effects in the chemical bond description with the indispensable factor—the atomicity. Also, the method bridges the atomic and molecular aspects of the chemical bond in precise multiparticle categories. A similar analysis may be carried out for the evolution of covalent into ionic bonds²⁶ in a more complex situation. Namely, by extending the single-particle basis in definition (16) of the field operators with, for example, 2p, etc. states, one can deal with more complex (e.g., C–C) bonds. In that situation, the subsequent analysis is still exact and feasible, but it is fully numerical in that case. Instead, one of our aims here was to exhibit the novel concepts/features of the problem in practically analytical terms. We should see a progress along these lines in the near future. In general, our

description uses complementary pictures in the quantum-mechanical sense (molecular vs atomic).

Method. Our analysis starts from the full form of a Hamiltonian in the second quantization, with all interaction terms between electrons on the lowest orbitals, that is

$$\begin{aligned} \hat{H} = & \epsilon_a \sum_{i\sigma} \hat{n}_{i\sigma} + \sum'_{ij\sigma} t_{ij} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \frac{1}{2} \sum'_{ji} K_{ij} \hat{n}_{i\sigma} \hat{n}_{j\sigma}, \\ & - \frac{1}{2} \sum'_{ij} J_{ij}^H \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j - \frac{1}{4} \hat{n}_i \hat{n}_j \right) \\ & + \frac{1}{2} \sum'_{ij} J'_{ij} (\hat{a}_{i\uparrow}^\dagger \hat{a}_{i\downarrow} \hat{a}_{j\downarrow} \hat{a}_{j\uparrow} + \text{H. c.}) \\ & + \frac{1}{2} \sum'_{ij} V_{ij} (\hat{n}_{i\sigma} + \hat{n}_{j\sigma}) (\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + \text{H. c.}) + \mathcal{H}_{\text{ion-ion}} \end{aligned} \quad (15)$$

where H.c. denotes the Hermitian conjugation, $\hat{a}_{i\sigma}$ ($\hat{a}_{i\sigma}^\dagger$) are Fermionic annihilation (creation) operators for state i and spin σ , $\hat{n}_{i\sigma} \equiv \hat{a}_{i\sigma}^\dagger \hat{a}_{i\sigma}$, and $\hat{n}_i \equiv \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} \equiv \hat{n}_{i\sigma} + \hat{n}_{i\bar{\sigma}}$. The spin operators are defined as $\hat{\mathbf{S}}_i \equiv \frac{1}{2} \sum_{\alpha\beta} \hat{a}_{i\alpha}^\dagger \boldsymbol{\sigma}_i^{\alpha\beta} \hat{a}_{i\beta}$ with $\{\sigma_i^{ab}\}$ representing Pauli matrices. The Hamiltonian contains the atomic and hopping parts (ϵ_a and t_{ij} respectively), the so-called Hubbard term $\propto U$, representing the intra-atomic interaction between the particles on the same atomic site i with opposite spins, the direct intersite Coulomb interaction $\propto K_{ij}$, Heisenberg exchange $\propto J_{ij}^H$, and the two-particle and the correlated hopping and intersite Coulomb terms ($\propto J'_{ij}$ and V_{ij} respectively). The last term describes the ion–ion Coulomb interaction, which is adopted here in its classical form. The microscopic parameters (ϵ_a , $t_{12} \equiv t$, U , $K_{12} = K$, $J_{12}^H = J'_{12}$, and $V_{12} = V$) are all calculated explicitly in the resultant correlated state by readjusting the single-particle wave function size contained in their expressions (for their analytic expressions see [Supporting Information](#)). The primed summations are taken for $i \neq j$. The evolution of the new introduced quantities: atomicity, true covalency, and ionicity, is analyzed in detail as a function of interatomic distance.

The Hamiltonian 15 was determined by defining first the field operators $\hat{\psi}_\sigma(\mathbf{r})$ and $\hat{\psi}_\sigma^\dagger(\mathbf{r})$, that is

$$\begin{cases} \hat{\psi}_\sigma(\mathbf{r}) = \sum_{i\sigma} w_i(\mathbf{r}) \chi_\sigma(i) \hat{a}_{i\sigma} \\ \hat{\psi}_\sigma^\dagger(\mathbf{r}) = \sum_{i\sigma} w_i(\mathbf{r}) \chi_\sigma^\dagger(i) \hat{a}_{i\sigma}^\dagger \end{cases} \quad (16)$$

where $\hat{a}_{i\sigma}$ ($\hat{a}_{i\sigma}^\dagger$) are the annihilation (creation) operators of the single-particle states $w_i(\mathbf{r}) \chi_\sigma(i)$ on atom $i = 1, 2$ with spin σ . Note that the single-particle basis is composed of the Hückel–Slater orbitals only; this restriction represents the only approximation here; the whole subsequent analysis and results are exact within these limitations. Those operators, in turn, lead to the expression (15) of $\hat{H}$ in a standard manner. To close the formal methodological part, the two-particle spin-singlet wave function is defined as²⁷

$$\psi_G(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \langle 0 | \hat{\psi}_1(\mathbf{r}_1) \hat{\psi}_2(\mathbf{r}_2) | \psi_G \rangle \quad (17)$$

where $|0\rangle$ is the universal vacuum state for particles and $|\psi_G\rangle$ is the ground state, both in Fock space. This relation provides an

equivalence of description both in terms of the two-particle wave function and the second-quantization language.

In Figure 4 we provide the flowchart of the numerical part of our analysis, which concerns mainly the determination of the

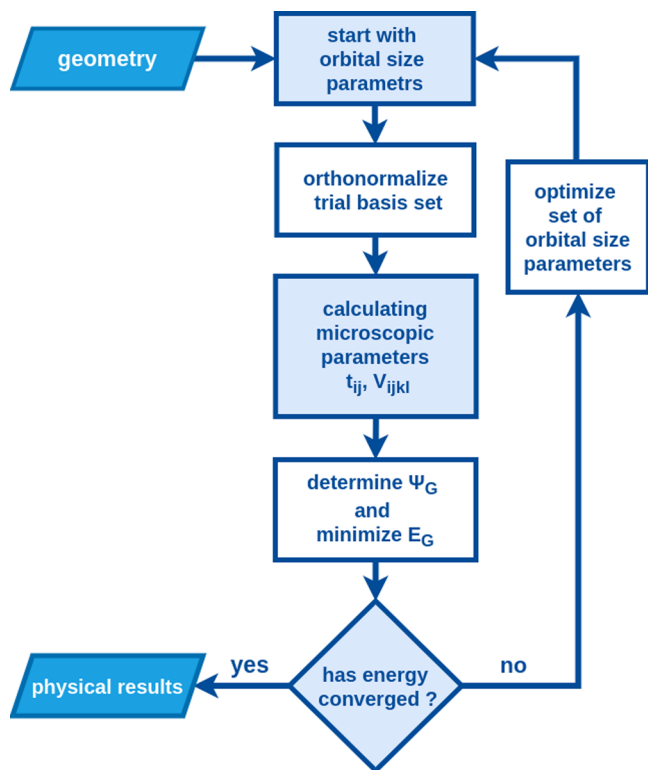


Figure 4. Flowchart of the EDABI method. The method is initialized by selection of a trial single-particle basis of wave functions (6) and subsequent diagonalization of the many-particle Hamiltonian (15). Optimization of the single-particle-state size leads to an explicit determination of the trial-wave function parameters, microscopic interaction and hopping parameters as well as ground-state energy, and explicit form of the many-particle wave function, all in the correlated interacting state for a given interatomic distance.

orbital size α^{-1} in the interacting (correlated) state and, in effect, of the optimal ground-state energy and all other bonding-state characteristics. The numerical sampling of the variational minimization with respect to α (inverse readjusted atomic-orbital size) is carried out by taking the step $\Delta\alpha = 0.01$. Further step diminishing does not influence significantly numerical values. The solution is exact with its method implemented in *Python* and *C++* languages, using additionally the QMT library.²⁸

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.2c02544>.

Additional methodological details, including step-by-step analytic calculations (PDF)

Transparent Peer Review report available (PDF)

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Notes

The authors declare no competing financial interest.

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Degree of Atomicity in the Chemical Bonding: Why Return to the H₂ Molecule?

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We analyze two-particle binding factors for the case of the H₂ molecule with the help of our original exact diagonalization *ab initio* approach. Explicitly, we redefine the many-particle covalency and ionicity factors as a function of interatomic distance. Insufficiency of those basic characteristics is stressed, and the concept of *atomicity* is introduced and corresponds to the Mott and Hubbard criteria concerning the electron localization in many-particle systems. This additional characteristic introduces atomic ingredients into the essentially molecular states and thus eliminates a spurious behavior of the standard covalency factor with the increasing interatomic distance, and also provides a physical reinterpretation of the chemical bond's nature.

topics: atomicity, hydrogen molecule, exact diagonalization *ab initio*, atomicity

1. Introduction

The concept of the chemical bond as the fundamental quantum-mechanical characteristic of molecules such as H₂ was firmly established by Heitler–London [1] in 1927. This, by today's standards, pioneering quantitative paper was based on the Hartree–Fock approximation for the two-particle wave function of the two electrons in an H₂ molecule. Later, the two-particle function has been expressed by the corresponding atomic 1s hydrogen wave functions in the form of symmetrized product of its spatial part with an antisymmetrized spin part, the latter reflecting the spin-singlet ground state. Such a selection of the component atomic wave functions represented a rather drastic approximation and has been corrected subsequently by selecting the superposition of those single-particle atomic wave functions into molecular single-particle wave functions centered on individual atoms, which have been subsequently brought into a proper two-particle form [2]. This whole procedure established a canonical viewpoint of the *covalent* bond, with a degree of ionicity (double occupancy of individual atoms) introduced *ad hoc* to it later (valence bond theory) [2]. The theory of bonding reached its mature form with an excellent series of papers by Kołos and Wolniewicz [3, 4], which included higher (virtually) excited states, supplemented with the nuclear vibrations [5] to a fully quantitative form, which has been subsequently tested experimentally since

the bonding in H₂ molecule represents one of the tests of quantum-mechanical-theory verification in quantum chemistry [6].

In this brief paper, we address, first of all, the question of why we must realize that there is a need to return to the problem origins of the bonding nature in the H₂ molecule. Namely, we have observed recently that the two-electron wave function, representing the single bond, composed of originally 1s electrons of hydrogen atoms, contains an inherent inconsistency when we interpret covalency in the standard manner [7, 8]. Explicitly, when starting from *an exact solution* of the Heitler–London problem (with proper molecular single-particle wave functions included at the start), we have detected that the covalency increases with the increasing distance between the nuclei, a clearly unphysical feature. As a subsidiary observation, we have noted that the Heitler–London (Hartree–Fock) two-electron wave function leads to a nonzero (actually, maximal) value of covalency in the limit of entirely separated atoms. Such inconsistencies have been brought to our attention the old concept of Mott [9] concerning electron localization in condensed matter physics (see also [10, 11]). In effect, we have decided to introduce the concept of *atomicity* in the context of correlated molecular electronic states [7]. This concept represents a novel nontrivial feature of the chemical bond since it is introduced as an external factor into an essentially molecular (collective) language of the covalent bonding, including also

ionicity. Hence, in this paper, we summarize and mainly interpret our recent results [7, 8], which, in our view, provide a connection between (correlated) states of small molecules and condensed matter physics, as well as delineate the essential difference between the two.

The structure of this paper is as follows. In Sect. 2, we briefly summarize our method, and in Sect. 3, regarded as the main part, we discuss our results and their meaning. This is followed in Sect. 4, in which we summarize and briefly overview our approach. In general, the aim of the paper is to supplement previous papers [7, 8] with a detailed discussion and interpretation of the results. Such a discussion may be of importance when the concept of *atomicity* is analyzed for more complicated bonds such as C–C in hydrocarbons. The connecting link between the condensed matter localization and *molecular atomicity* may be then applied to other nano-systems as well [11].

2. Method

Our approach is based on the exact diagonalization *ab initio* (EDABI) method, which has been proposed and developed in our group [12, 13]. Here we use this method to provide complementary bonding characteristics on the example of the H₂ molecule. The starting Hamiltonian, containing all Coulomb interactions, formulated in the second quantization language, is of the form

$$\begin{aligned} \hat{\mathcal{H}} = & \epsilon_a \sum_i \hat{n}_{i\sigma} + \sum'_{ij\sigma} t_{ij} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \\ & + \frac{1}{2} \sum'_{ij} K_{ij} \hat{n}_i \hat{n}_j - \frac{1}{2} \sum'_{ij} J_{ij}^H \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j - \frac{1}{4} \hat{n}_i \hat{n}_j \right) \\ & + \frac{1}{2} \sum'_{ij} J'_{ij} (\hat{a}_{i\uparrow}^\dagger \hat{a}_{i\downarrow}^\dagger \hat{a}_{j\downarrow} \hat{a}_{j\uparrow} + \text{h.c.}) \\ & + \frac{1}{2} \sum'_{ij} V_{ij} (\hat{n}_{i\sigma} + \hat{n}_{j\sigma}) (\hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + \text{h.c.}) + \mathcal{H}_{\text{ion-ion}}, \end{aligned} \quad (1)$$

where h.c. denotes the Hermitian conjugation; $\hat{a}_{i\sigma}$ ($\hat{a}_{i\sigma}^\dagger$) are fermionic annihilation (creation) operators for state i and spin σ ; $\hat{n}_{i\sigma} \equiv \hat{a}_{i\sigma}^\dagger \hat{a}_{i\sigma}$ and $\hat{n}_i \equiv \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} \equiv \hat{n}_{i\sigma} + \hat{n}_{i\bar{\sigma}}$. The spin operators are defined as $\hat{\mathbf{S}}_i \equiv \frac{1}{2} \sum_{\alpha\beta} \hat{a}_{i\alpha}^\dagger \boldsymbol{\sigma}_i^{\alpha\beta} \hat{a}_{i\beta}$ with σ_i representing Pauli matrices. The primed summations mean that $i \neq j$. The Hamiltonian contains the atomic and hopping parts ($\propto \epsilon_a$ and t_{ij} , respectively), the so-called Hubbard term $\propto U$ representing the intra-atomic interaction between the particles on the same atomic site i with opposite spins, the direct intersite Coulomb interaction $\propto K_{ij}$, Heisenberg exchange $\propto J_{ij}^H$, and the two-particle and the correlated hopping terms ($\propto J'_{ij}$ and V_{ij} , respectively). The last term describes the ion-ion Coulomb interaction, which is adopted here in its classical form.

By way of diagonalization of Hamiltonian (1), one can write ground state energy with the ground state two-particle wave function, obtained in the form $\psi_G(\mathbf{r}_1, \mathbf{r}_2) = \psi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) + \psi_{\text{ion}}(\mathbf{r}_1, \mathbf{r}_2)$, where ionic and covalent parts are

$$\begin{aligned} \psi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) = & \frac{2(t+V)}{\sqrt{2D(D-U+K)}} \left[w_1(\mathbf{r}_1)w_2(\mathbf{r}_2) \right. \\ & \left. + w_1(\mathbf{r}_2)w_2(\mathbf{r}_1) \right] \left[\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2) \right], \end{aligned} \quad (2)$$

$$\begin{aligned} \psi_{\text{ion}}(\mathbf{r}_1, \mathbf{r}_2) = & -\frac{1}{2} \sqrt{\frac{D-U+K}{\sqrt{2D}}} \left[w_1(\mathbf{r}_1)w_1(\mathbf{r}_2) \right. \\ & \left. + w_2(\mathbf{r}_2)w_2(\mathbf{r}_1) \right] \left[\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2) \right], \end{aligned} \quad (3)$$

with

$$D \equiv \sqrt{(U-K)^2 + 16(t+V)^2}, \quad (4)$$

and

$$w_{i\sigma}(\mathbf{r}) = \beta \left(\phi_{i\sigma}(\mathbf{r}) - \gamma \phi_{j\sigma}(\mathbf{r}) \right), \quad (5)$$

with $i = 1, j = 2$ or $i = 2, j = 1$, in this case. The two functions are molecular functions and come out naturally within our method, in which the two neighboring atomic functions $\phi_i(\mathbf{r})$ are mixed, with β and γ as mixing parameters. These atomic functions can be in the form of Slater or Gaussian form (Slater or Gaussian type orbitals, STO or GTO). Furthermore, (2) and (3) can be rewritten, with the use of (5), in the following way [7]

$$\begin{aligned} \psi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) = & \left(C\beta^2(1+\gamma^2) - 2\gamma I\beta^2 \right) \left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \right. \\ & \left. + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2) \right] \left[\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2) \right], \end{aligned} \quad (6)$$

and

$$\begin{aligned} \psi_{\text{ion}}(\mathbf{r}_1, \mathbf{r}_2) = & \left(I\beta^2(1-\gamma^2) - 2\gamma C\beta^2 \right) \left[\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) \right. \\ & \left. + \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \right] \left[\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2) \right], \end{aligned} \quad (7)$$

where C and I are the same coefficients as in (2) and (3), respectively. Now the covalency, and ionicity are defined as the squared coefficients before the functions (6) and (7).

Parenthetically, for the sake of comparison, one can write postulated VB two-particle wave functions

$$\begin{aligned} \psi_{\text{cov}}^{\text{VB}}(\mathbf{r}_1, \mathbf{r}_2) = & \frac{\left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2) \right]}{\sqrt{2(1+S^2)}} \\ & \times \frac{1}{\sqrt{2}} \left[\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2) \right], \end{aligned} \quad (8)$$

and

$$\begin{aligned} \psi_{\text{ion}}^{\text{VB}}(\mathbf{r}_1, \mathbf{r}_2) = & \left[\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \right] \\ & \times \frac{1}{\sqrt{2}} \left[\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2) \right], \end{aligned} \quad (9)$$

where S is the overlap between the neighboring atomic wave functions. However, the total wave function, consisting of the sum of (8) and (9), has not been obtained directly as a solution of the respective Schrödinger equation, whereas in our approach, its form comes out explicitly from our exact solution and represents the exact treatment of the Heitler–London problem.

Based on these functions, we redefine below ionicity and covalency [8] and define atomicity [7], the last being the complementary characteristic to the former two.

A remark is in place at this point. As said above, the two-electron component wave functions (6) and (7) have formally the same form as their VB correspondents (8) and (9), albeit with two principal differences. First, the coefficients before the covalent and ionic parts, ψ_{cov} and ψ_{ion} , are different as they contain *all* Coulomb-interaction terms between the particles composing the bond. Second, the orbital size (α^{-1}) of the original atomic wave functions composing those functions is adjusted in the resultant two-particle ground state. These two factors, in addition to the exact expression for the two-particle wave function, are the qualitative differences with the original Heitler–London theory.

In Sect. 3, we discuss our results after minimizing the ground state energy, $E_G[\psi_G(\alpha)] \equiv \langle \psi_G(\alpha) | \hat{\mathcal{H}} | \psi_G(\alpha) \rangle / \langle \psi_G(\alpha) | \psi_G(\alpha) \rangle$, with respect to α , and explicitly evaluating the microscopic parameters for the optimal value of $\alpha = \alpha_0$.

3. Results and discussion

We now proceed with the presentation of our results, followed up by a discussion on them. In Fig. 1, we illustrate the interatomic distance, R , and dependence of the quantities with marked Hubbard and Mott criteria of localization (upper and lower red points, respectively). The Hubbard criterion (purple line) delineates the point where the kinetic-to-interaction ratio, $2|t+V|/(U-K)$, takes the value of unity. The Mott criterion, in turn, describes the point where the atomic orbital size is of the same magnitude as the interatomic distance. The right-hand-side region (shaded) then describes the regime, where both the interaction dominates over the electron kinetic energy (according to the Hubbard criterion) and, simultaneously, the atomic size in the correlated state is decisively smaller than the interatomic distance. Obviously, those criteria, crucial for the Mott–Hubbard localization in condensed matter, are only of qualitative nature in the case of molecules. They represent the finite-system situation, and therefore, any sharp delocalization–localization transformation of molecular states into their atomic correspondents is ruled out. Before discussing the details, we show that the coefficients attached to the wave-function parts (2) and (3) represent the standard definition of covalency and

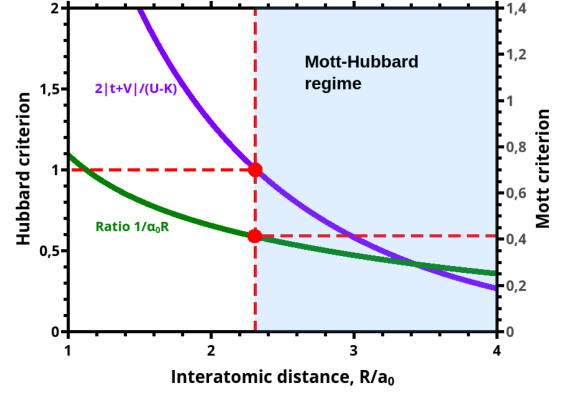


Fig. 1. Mott (green, lower) and Hubbard (purple, upper) lines with the marked corresponding Mott and Hubbard criteria of localization. The shaded area to the right of $R = R_{\text{Mott}}$ represents the region with steadily increasing atomicity with increasing R . For details see the main text.

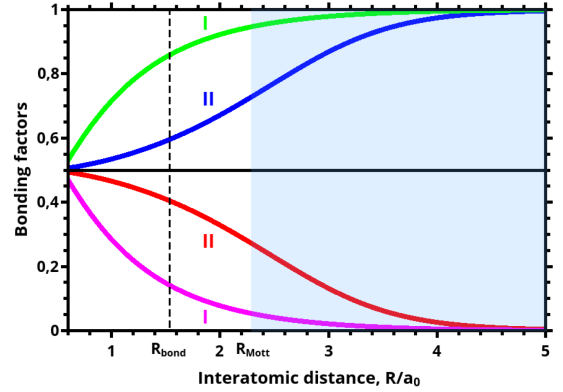


Fig. 2. Comparison of starting binding factors (ionicity and standard covalency) vs interatomic distance. Those microscopic parameters are determined, respectively: from Hubbard model — curves I, extended Hubbard model — curves II. The shaded area corresponds to the Mott–Hubbard (“Mottness”) regime, where the interactions dominate over the kinetic energy particles (for details see [7, 8]). The broken vertical line marks the equilibrium bond length $R_{\text{Bond}} = 1.43a_0$.

ionicity, as is evident from the form of the corresponding component wave functions (second factors of the products in (6) and (7), respectively). Their numerical values are displayed in Fig. 2. For the sake of completeness, we have included in Fig. 2 also the results for the full solutions (curves labeled by I) and those corresponding to the Hubbard model solutions (curves II). Parenthetically, the curves II describe the situation when we disregard all intersite Coulomb interaction and retain only the dominant term with intraatomic interaction $\sim U$. In either case, the covalency behaves unphysically with the interatomic distance $R \rightarrow \infty$ ($R > R_{\text{Mott}}$).

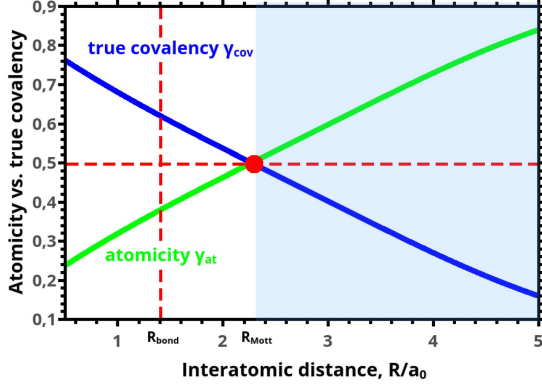


Fig. 3. Participation of true covalency and atomicity in the resultant correlated state of electrons in H_2 . Note that the two curves cross the marked point, which corresponds accurately to the one shown in Fig. 1.

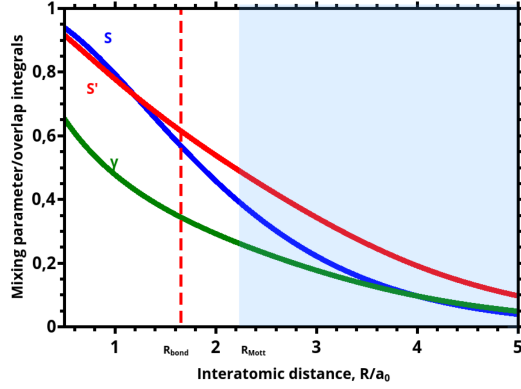


Fig. 4. Single-particle mixing parameter γ , overlap integral without orbital size renormalization S , and orbital size calculated for renormalized orbital size S' versus interatomic distance R . They evolve continuously as a function of interatomic distance. The dashed vertical line marks, as in all previous figures, the equilibrium bond length, whereas the shaded area represent the “*Mottness*” regime.

To restore physical meaning to the *covalency*, we make use of our earlier observation that in the $R \rightarrow \infty$ limit, the Heitler–London wave function reduces to the Slater determinant of the corresponding atomic states, with no ionicity, as it represents the probability amplitude of double occupancy on the same atom. We have proposed to exclude the *atomicity* γ_{at} from the covalency presented in Fig. 3 by extracting from the corresponding expression (6) for covalency the part taken for $\gamma = 0$ at the given R (not only in the atomic limit). As a result, we get the *true covalency versus atomicity*, both as a function of R , depicted in Fig. 3. The ionicity remains without change since it expresses the complementary factor of bonding — double occupancy. One should stress the fundamental difference between

TABLE I

Binding energy of H_2 calculated with restricted Hartree–Fock (RHF), configurational interaction (CI), and EDABI (with Hubbard Hamiltonian (HM-EDABI) and with extended Hamiltonian (EM-EDABI)) methods and percentage difference with the exact Kołos–Wolniewicz (K–W) results [4].

	Binding energy [eV]	Difference with K–W [%]
RHF	−3.5963	5.6
Full CI	−4.3824	0.6
HM-EDABI	−3.9783	3.1
EM-EDABI	−4.0749	2.7

TABLE II

Bond length and correlation energy (calculated as $E_{HF} - E$, where E_{HF} is Hartree–Fock energy and E is energy in appropriate method) for H_2 calculated with restricted Hartree–Fock (RHF), configurational interaction (CI), and EDABI (with Hubbard Hamiltonian (HM-EDABI) and with extended Hamiltonian (EM-EDABI)) methods.

	Bond length (a_0)	Correlation energy [eV]
RHF	1.450	N/A
Full CI	1.501	−0.5136
HM-EDABI	1.442	−0.0978
EM-EDABI	1.430	−0.1706

TABLE III

Binding factors at $R = R_{Bond}$ calculated for many-particle wave function from extended second quantized Hamiltonian and Hubbard Hamiltonian, as well as for single-particle wave function from valence bond (VB) theory (with and without renormalizing orbital size).

	Covalency	Ionicity
full Hubbard model	0.59	0.41
Hubbard model	0.86	0.14
VB theory	0.52	0.48
VB theory (renormalized)	0.63	0.37
space bonding descriptor [14]	0.57	0.43

TABLE IV

True binding characteristics for H_2 at equilibrium point of R with subtracted atomicity. Note that in Table III the atomicity is an integral part of the standard covalency.

True covalency	Atomicity	Ionicity
0.48	0.19	0.33

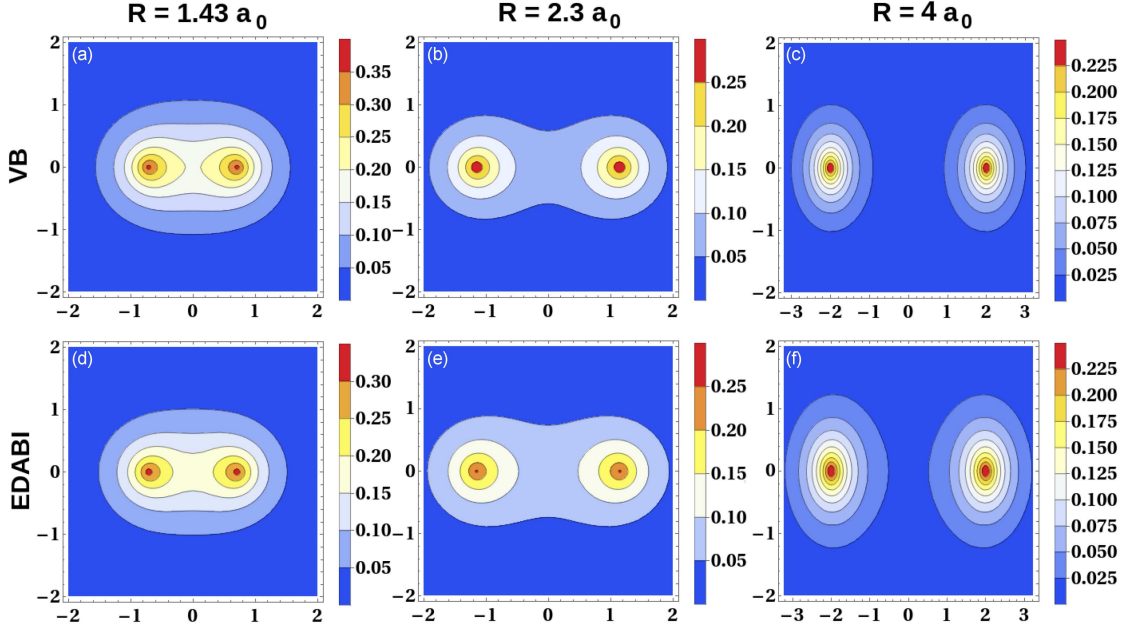


Fig. 5. Probability density profiles according to valence bond (VB) approach panels (a)–(c)), as well as those taking the two-particle wave functions (2) and (3) (panels (d)–(f)). The interatomic distance R is specified.

the covalency and ionicity factors, γ_{cov} and γ_{ion} , shown in Fig. 2 and those exhibited in Fig. 3. In the former case, we have that $\gamma_{\text{cov}} + \gamma_{\text{ion}} = 1$, whereas in the present situation, $\gamma_{\text{cov}} + \gamma_{\text{ion}} + \gamma_{\text{at}} = 1$ (for details, see [7]). It is remarkable that the Mott–Hubbard criterion for localization meets the point, where the atomicity γ_{at} and redefined covalency γ_{cov} are equal. Obviously, for larger R values, the atomicity prevails, whereas the ionicity γ_{ion} (not shown) decreases steadily to zero.

To illustrate our results by way of showing that the onset of atomicity is a collective phenomenon, i.e., induced by electron–electron Coulomb interaction, we have plotted in Fig. 4 the single-particle characteristics γ as an admixture of the neighboring and readjusted (in the correlated state) wave function, while S and S' are overlap integrals, for readjusted (S') and original s -state (S) wave functions, respectively. All those functions diminish gradually with the increasing R , without showing any sign of difference at either $R = R_{\text{Bond}}$ and $R = R_{\text{Mott}}$. In other words, the atomicity appears as a result of interelectronic interaction induced by the correlations.

To summarize, as well as to put our results in a broader perspective, we have listed selected properties of our calculations/computations in Tables I and II. There, we have specified some standard quantities for the equilibrium state of the H_2 molecule (cf. Table I), as well as singled out the bond characteristics (Table II). Additionally, we have supplemented these results with the true covalency, atomicity, and ionicity factors in Tables III and IV.

4. Conclusions

The principal concept introduced in our approach [8] is the concept of *atomicity* in a nominally covalent bond of H_2 (albeit also with a non-trivial degree of ionicity). One should be aware of the fact that hydrogen molecule, in the hypothetical so far limit $R \rightarrow \infty$, composed of separated atoms, is in an incoherent quantum–mechanical state. Here we introduce such an incoherent admixture in the situation of still finite interatomic distance. This means that the entangled state of the two electrons in the correlated molecular state is then partially disentangled. One should still examine whether this quantum-coherence limitation appears only for bound states, i.e., it is present also at a finite distance when the particles interact, which is not the case with photons at any distance [15]. Until our last statement is proved, our proposal of atomicity in bound molecular states at a finite distance should be regarded as intuitive in nature, even though it helps to remove the principal inconsistency in the evolution of the covalency as a function of interatomic distance.

Finally, the overall behavior of the H_2 system is illustrated in Fig. 5, where the probability density profiles are shown for the three interatomic distances specified: at equilibrium bond distance ($R = 1.43a_0$), at the Mott–Hubbard boundary ($R = 2.3a_0$), and in the asymptotic regime of large distances ($R = 4a_0$). The density profiles are artificially distorted from their almost spherical shapes by choice of scale to expose the details of the density isolines in that case. One sees the quasi-atomic

character of the wave functions for $R > R_{\text{Mott}}$ in either approach, VB or EDABI. Nevertheless, the principal difference between the two is as follows. The limitation of the Heitler–London approach is caused by the selection of atomic $1s$ wave function to construct the two-particle state and the choice of the latter for the purely covalent state. In our case (EDABI), the single-particle states (molecular orbitals) with the adjusted size are taken — this effect is mainly due to the orbital size renormalization by their interaction. Additionally, the form of the two-particle wave function is more general as it contains also the ionic part.

Acknowledgments

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Interparticle correlations and chemical bonding from physical side: Covalency vs atomicity and ionicity

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Abstract

In this chapter we reexamine the concept of *covalency* and *ionicity* on example of the simplest molecules. First, starting from the exact expression for the two-particle wave function in the case of H₂ molecule within the Heitler–London model, we demonstrate an unphysical behavior of the covalency at large interatomic distance which, within standard definition, reaches the maximal value in the limit of separated atoms. Second, we correct this deficiency by introducing the concept of *atomicity*, with the help of which, we define the *true* (intrinsic) *covalency*, as well as retain the precise concept of *ionicity*. We connect the introduced atomicity to the onset of Mott–Hubbard

localization, adopted here from the well-established notion in the condensed matter. The evolution from the molecular to atomic states develops rapidly with interatomic distance beyond the localization threshold. This brief overview is intended as pedagogical in nature, nonetheless is analyzed quantitatively for the case of H_2 molecule. At the end, we outline a similar-type of model for the related case of the hydrogen bond on example of adenine–thymine pair. Methodologically, the approach is based on combining the first (wave mechanics) and second quantization into a single scheme of formal description.



1. Motivation

The quantum mechanical concept of the chemical bond was introduced in the quantitative way on example of H_2 by Heitler and London (HL)¹ (see also related papers^{2–4}). This theory was formulated only a year after the wave mechanics had been rigorously established by Schrödinger for the discrete states of single hydrogen atom and subsequently extended by Dirac⁵ by introducing the indistinguishability principle to the many-particle wave function. The HL approach was based on what is now known as the Hartree–Fock two-particle wave function (strictly speaking, solely on its orbital part). This wave function is at present taken of the following spin-singlet form

$$\psi_{12}(\mathbf{r}, \mathbf{r}) = \frac{1}{\sqrt{2(1+S^2)}} [\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2) + \varphi_1(\mathbf{r}_2)\varphi_2(\mathbf{r}_1)] [\chi_{\uparrow}(1)\chi_{\downarrow}(2) - \chi_{\downarrow}(1)\chi_{\uparrow}(2)]. \quad (1)$$

The wave function originally contained hydrogen atomic wave functions $\varphi_1(\mathbf{r}) = \varphi(\mathbf{r} - \mathbf{R}_1)$ and $\varphi_2(\mathbf{r}) = \varphi(\mathbf{r} - \mathbf{R}_2)$ centered at H_2 nuclei positions $\mathbf{R}_1$ and $\mathbf{R}_2$, respectively. They represent the hydrogen $1s$ orbital wave functions, whereas $\chi_{\sigma}(i)$ are the corresponding spin functions with spin $\sigma = \uparrow, \downarrow$ and $i \equiv \mathbf{R}_i$. This form (1) is a result of an ad hoc assumption and expresses the principle of antisymmetry with respect to transposition of the quantum numbers (i, σ) ; $S = \langle \varphi_1 | \varphi_2 \rangle$ is the overlap of the functions. In general, the evolution of the wave function form in time is schematically summarized in Fig. 1 (see Fig. 1 caption for detailed description). The ansatz taken to define the form (1) was later extended by selecting more involved wave functions and has resulted in the full configuration interaction (FCI) formulation,⁶ involving also the most important virtually excited states. Nowadays, it comprises a whole discipline of advanced computational chemistry, including also the density functional theory

Two-particle wave functions			
Ansatz	Hartree-Fock I	$A[\varphi_A(\mathbf{r}_1)\chi_{\uparrow}(1)\varphi_B(\mathbf{r}_2)\chi_{\downarrow}(2)$ $- \varphi_A(\mathbf{r}_2)\chi_{\uparrow}(2)\varphi_B(\mathbf{r}_1)\chi_{\downarrow}(1)]$ $\equiv \varphi_A(\mathbf{r}_1)\varphi_B(\mathbf{r}_2)[\chi_{\uparrow}(1)\chi_{\downarrow}(2) - \chi_{\downarrow}(1)\chi_{\uparrow}(2)]$	antysymmetrized spinorbitals
	Heitler-London (1927)	$[\varphi_A(\mathbf{r}_1)\varphi_B(\mathbf{r}_2) \pm \varphi_A(\mathbf{r}_2)\varphi_B(\mathbf{r}_1)]$	covalent part
	Spin Coupled Valence Bond (Hartree-Fock II)	$A[\varphi_A(\mathbf{r}_1)\varphi_B(\mathbf{r}_2) \pm \varphi_A(\mathbf{r}_2)\varphi_B(\mathbf{r}_1)]$ $+ (1 - A)[\varphi_A(\mathbf{r}_1)\varphi_A(\mathbf{r}_2) \pm \varphi_B(\mathbf{r}_2)\varphi_B(\mathbf{r}_1)]$ $\times [\chi_{\uparrow}(1)\chi_{\downarrow}(2) \mp \chi_{\downarrow}(1)\chi_{\uparrow}(2)]$	covalent part ionic part spin-part
	Coulson-Fisher (1949)	$A[\Phi_A(\mathbf{r}_1)\Phi_B(\mathbf{r}_2) \pm \Phi_A(\mathbf{r}_2)\Phi_B(\mathbf{r}_1)]$	covalent part
Configurational Interaction		$\sum_{\{i\}} c_i \det(\varphi_i(\mathbf{r}))$	multiple Slater determinants
Exact Diagonalization Ab Initio		$C[w_A(\mathbf{r}_1)w_B(\mathbf{r}_2) \pm w_A(\mathbf{r}_2)w_B(\mathbf{r}_1)]$ $+ I[w_A(\mathbf{r}_1)w_A(\mathbf{r}_2) \pm w_B(\mathbf{r}_2)w_B(\mathbf{r}_1)]$ $\times [\chi_{\uparrow}(1)\chi_{\downarrow}(2) \mp \chi_{\downarrow}(1)\chi_{\uparrow}(2)]$	covalent part ionic part spin-part

$\varphi_i(\mathbf{r})$ - atomic wave function

$$\begin{aligned} \Phi_i(\mathbf{r}) &= \varphi_i(\mathbf{r}) + \lambda \varphi_{i+1}(\mathbf{r}) \\ w_i(\mathbf{r}) &= \beta[\varphi_i(\mathbf{r}) + \gamma \varphi_{i+1}(\mathbf{r})] \end{aligned}$$

- two equivalent variants of molecular orbitals (MO)

Fig. 1 The evolution of the form of the two-particle wave function starting from original (Hartree–Fock I), through Heitler–London (originally without the spin part), followed by spin-coupled valence bond from Coulson and Fisher, as well as the configuration interaction form (the last represents linear combination of Slater determinants for possible occupancies). The *bottom line* composes our result obtained on the basis of our EDABI method.

(DFT) calculations, etc.⁷ It is this stage at which the unique calculations of Kołos and Wolniewicz resulted in practically exact results for the H_2 molecule ground state.^{8,9} Such a procedure also requires, as a must, replacement of the original atomic wave functions $\{\varphi_i\}$ in (1) by appropriate molecular orbitals $\{\Phi_{ij}\}$.⁴

Our approach begins from a different starting point.^{10–12} Namely, we combine the wave (1st quantization) and particle (2nd quantization) languages of electron states description, composing a single chemical bond (i.e., of two-electron states) and show how the *ionicity* arises in a natural manner and, what is crucial, the importance of the introduced concept of *atomicity* in the bonding state, so that the *true* (or *intrinsic*) *covalency* can be

quantitatively defined. In this manner, an intrinsic inconsistency in the standard definition of covalency is removed. Furthermore, the full Hamiltonian with all two-particle interactions can be written in a compact form, as well as an accurate analytic expression for the two-particle wave function is explicitly provided. This formulation represents the exact solution of the HL model and constitutes a crucial step forward in a systematic analysis of the bonding properties of more complex molecular systems. In particular, the limiting situation of separate atoms is recovered correctly, i.e., when the state of indistinguishable (bound) electrons transform into that of their distinguishable (atomic) correspondents. Some of the possible extensions of our approach, discussed here in detail for H_2 molecule, are briefly characterized at the end.



2. Method: First and second quantization combined

The principal features of our original *exact diagonalization ab initio* (EDABI) method and interpretation of physical results are carried out here on example of H_2 molecule. Thus the starting point are the electronic states of the two electrons that originate from parent hydrogen atoms, each placed in $1s$ atomic Slater state. We neglect a possibility of virtual electronic transitions to $2s$ and higher excited states and would like to study an adiabatic evolution of those atomic states into the two-particle molecular state (forming the bond) with the decreasing interatomic distance R . In the particle (second quantization) language, the situation can be described by starting from the field operator language in which the particles are represented by the field operator of the form

$$\hat{\psi}_{\sigma}(\mathbf{r}) = w_1(\mathbf{r})\chi_{\sigma}(1)\hat{a}_{1\sigma} + w_2(\mathbf{r})\chi_{\sigma}(2)\hat{a}_{2\sigma} \quad (2)$$

in which the molecular (Wannier) orthogonalized and normalized wave functions $\{w_{i\sigma}(\mathbf{r}) \equiv w_{\sigma}(\mathbf{r} - \mathbf{R}_i)\}_{i=1,2}$ are defined as

$$w_{i\sigma}(\mathbf{r}) = \beta[\varphi_{i\sigma}(\mathbf{r}) - \gamma\varphi_{j\sigma}(\mathbf{r})] = \beta[\phi_i(\mathbf{r})\chi_{\sigma}(i) - \gamma\phi_j(\mathbf{r})\chi_{\sigma}(j)], \quad (3)$$

where β and γ are mixing coefficients for the state centered on site i with that centered on the neighboring site j . We should stress that the selection of the hybridized (Wannier) basis is a natural choice here as only then the anticommutators between the creation and annihilation operators have a universal form (see below).

For the starting atomic states we select Slater-type orbitals $\phi_{i\sigma} = \sqrt{\alpha^3/\pi} \exp[-\alpha|\mathbf{r} - \mathbf{R}_i|] \chi_\sigma$ in which α^{-1} is an adjustable in correlated state size of the orbital (see below). The explicit form of the mixing coefficient is

$$\beta = \frac{1}{\sqrt{2}} \left[\frac{1}{1 - S^2} + \frac{1}{\sqrt{1 - S^2}} \right] \quad (4)$$

where $\gamma^2 \equiv (1 - \beta^2)/\beta$.

One methodological remark is in place here. Namely, the form (2) of the field operator is approximate, as the sum over states $\{w_i(\mathbf{r})\}$ should, in principle cover **all** higher excited states, i.e., $\{\phi_i(\mathbf{r})\}$ should represent a complete set of hydrogen atomic states or the corresponding full basis of molecular states. For the sake of argument clarity the basis is limited to (2). However, to optimize the truncated energy of the interacting (correlated) two-particle state we minimize the ground state energy E_G additionally with respect to α . In this way, the orbital size is readjusted in the resultant interacting (correlated) state. Note that incompleteness of the basis $\{w_i(\mathbf{r})\}$ in defining the field operator (2) means that we reduce here the problem to the HL type of model, albeit we amend it with the single-particle basis optimization (through adjustment of α in the resultant state) and reanalyze the exact solution of the model in the second quantization representation (i.e., going systematically beyond the original Hartree–Fock-type solution).

For the selected starting single-particle orthogonalized basis $\{w_\sigma(\mathbf{r})\}$ we construct the system Hamiltonian in the second-quantized representation which is

$$\begin{aligned} \hat{\mathcal{H}} = & \sum_{\sigma} \int d^3\mathbf{r} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \left[-\frac{\hbar}{2m} \nabla^2 + V(\mathbf{r}) \right] \hat{\psi}_{\sigma}(\mathbf{r}) \\ & + \frac{1}{2} \sum_{\sigma\sigma'} \int d^3\mathbf{r} d^3\mathbf{r}' \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}_{\sigma'}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}') \end{aligned} \quad (5)$$

where the first term represents the single-particle part containing both kinetic energy of electron and the original atomic potential $V(\mathbf{r})$ coming from both protons. The second term expresses two-particle Coulomb repulsion. Upon inserting expression (2) for $\hat{\psi}_{\sigma}(\mathbf{r})$ and the corresponding one for $\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \equiv [\hat{\psi}_{\sigma}(\mathbf{r})]^{\dagger}$ we obtain the full Hamiltonian in terms of creation $(\hat{a}_{i\sigma}^{\dagger})$ and annihilation $(\hat{a}_{i\sigma})$ operators, that takes the following form

$$\begin{aligned}
\hat{\mathcal{H}} = & \sum_{i\sigma} \epsilon_i \hat{n}_{i\sigma} + \sum'_{ij\sigma} t_{ij} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + \sum_i U_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \frac{1}{2} \sum'_{ij\sigma\sigma'} K_{ij} \hat{n}_{i\sigma} \hat{n}_{j\sigma'} \\
& - \frac{1}{2} \sum'_{ij} J_{ij}^H \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j - \frac{1}{4} \hat{n}_i \hat{n}_j \right) + \frac{1}{2} \sum'_{ij} J'_{ij} \left(\hat{a}_{i\uparrow}^\dagger \hat{a}_{i\downarrow}^\dagger \hat{a}_{j\downarrow} \hat{a}_{j\uparrow} + \text{H.c.} \right) \quad (6) \\
& + \frac{1}{2} \sum'_{ij} V_{ij} (\hat{n}_{i\sigma} + \hat{n}_{j\sigma}) \left(\hat{a}_{i\bar{\sigma}}^\dagger \hat{a}_{j\bar{\sigma}} + \text{H.c.} \right) + \mathcal{H}_{\text{ion-ion}},
\end{aligned}$$

In this expression the first term expresses the atomic energy of electrons, whereas $\hat{n}_{i\sigma} \equiv \hat{a}_{i\sigma}^\dagger \hat{a}_{i\sigma}$ and $\hat{\mathbf{S}}_i \equiv \left(\hat{a}_{i\uparrow}^\dagger \hat{a}_{i\downarrow}, \hat{a}_{i\downarrow}^\dagger \hat{a}_{i\uparrow}, \frac{1}{2} (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow}) \right)$ are the particle-number- and spin-operators, respectively. The second term represents the hopping energy of electrons between the sites (with $i \neq j$); it expresses the energy contribution coming from resonant hops of individual carriers between the sites (prime means $i \neq j$). The third term represents the intra-atomic part of the Coulomb repulsion between the electrons on the same atom with opposite spins, whereas the fourth contains the corresponding part of the intersite Coulomb (Hubbard) interaction. The next three terms represent direct (Heisenberg) exchange interaction, pair-particle hopping between the sites and the so-called correlated hopping, respectively. The last three terms are usually of lesser importance in correlated systems. The microscopic parameters are integrals containing the Slater single-particle Wannier functions in a standard manner (cf. Appendix in Ref. 13) Finally, $\mathcal{H}_{\text{ion-ion}}$ expresses the classical Coulomb interaction between the nuclei (protons in the case of H_2 molecule). Note also that the microscopic parameters ϵ_a , t_{ij} , U , K_{ij} , J_{ij}^H , J'_{ij} , and V_{ij} can be calculated analytically for $1s$ orbitals, as shown by Slater¹⁴ (see also Ref. 10); they will be evaluated explicitly here in the interacting (correlated) state (for i.e., readjusted orbital size).

The next step in process of solving the Hamiltonian is the diagonalization of (6) in the Fock space for given of microscopic parameters. For that purpose, we select a set of trial orthogonal and normalized states for two electrons which in this case of H_2 molecule are

$$\left\{ \begin{array}{l} |1\rangle = \hat{a}_{1\uparrow}^\dagger \hat{a}_{2\uparrow}^\dagger |0\rangle, \\ |2\rangle = \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\downarrow}^\dagger |0\rangle, \\ |3\rangle = \frac{1}{\sqrt{2}} \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle, \\ |4\rangle = \frac{1}{\sqrt{2}} \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger - \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle, \\ |5\rangle = \frac{1}{\sqrt{2}} \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger + \hat{a}_{2\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle, \\ |6\rangle = \frac{1}{\sqrt{2}} \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger - \hat{a}_{2\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle. \end{array} \right. \quad (7)$$

Note that for N sites with N_e electrons, we have $\binom{2N}{N_e}$ two-particle states, which is equal to six for $N = 2$ sites and $N_e = 2$ electrons. The diagonalized state thus contains three spin-triplet states (with the total-spin S^Z component equal to $S^Z = 1, -1$, and 0 , respectively) and three spin-singlet states. The basis is complete for this model with two $1s$ -type states (HL model) and for Hamiltonian (6) can be brought to the 6×6 matrix form, which splits into three 1×1 irreducible parts representing three separate spin-triplet states with eigenenergy

$$\lambda_1 = \lambda_2 = \lambda_3 = \epsilon_1 + \epsilon_2 + K - J^H, \quad (8)$$

as well as 3×3 submatrix of mixed spin-singlet states, which is of the form

$$\hat{\mathcal{H}} = \begin{pmatrix} \epsilon + K + J^H & 2(t + V) & 0 \\ 2(t + V) & 2\epsilon + J + U & \frac{1}{2}(U_1 - U_2) \\ 0 & \frac{1}{2}(U_1 - U_2) & 2\epsilon + U - J^H \end{pmatrix}, \quad (9)$$

with $\epsilon_a \equiv (\epsilon_1 + \epsilon_2)/2$ and $U \equiv (U_1 + U_2)/2$. In the case of two identical atoms (H_2 molecule) this matrix can be diagonalized analytically (since $U_1 = U_2 = U$), with the eigenvalues $\lambda_1 = \lambda_2 = \lambda_3 = 2\epsilon_a + K - J$ for the states $|1\rangle = |\lambda_1\rangle$, $|2\rangle = |\lambda_2\rangle$, and $|3\rangle = |\lambda_3\rangle$ and $\lambda_6 = 2\epsilon_a + U - J$ for the state $|6\rangle = |\lambda_6\rangle$. However, the states $|4\rangle$ and $|5\rangle$ are intermixed and in the case $\epsilon_1 = \epsilon_2$, $U_1 = U_2$ (the case of H_2 molecule) the eigenvalues can be written in an analytic form, namely¹⁵

$$\lambda_{4,5} \equiv \lambda_{\pm} = 2\epsilon_a + \frac{1}{2}(U + K) \pm \frac{1}{2}[(U - K)^2 + 16(t + V)^2]^{\frac{1}{2}}. \quad (10)$$

The corresponding two eigenstates, in turn, have the following explicit form

$$|\lambda_{4,5}\rangle \equiv |\lambda_{\pm}\rangle = [2D(D \pm U \mp K)]^{-\frac{1}{2}}\{4(t + V)|4\rangle \pm (D \pm U \mp K)|5\rangle\}, \quad (11)$$

with $D \equiv [(D - K)^2 + 16(t + V)^2]^{\frac{1}{2}}$. The last two states are the most interesting here, because $|\lambda_{-}\rangle$ is the ground state; all the remaining states are excited states. We see that the intersite spin-singlet states $|\lambda_{\pm}\rangle$ have an admixture of symmetric ionic state $|5\rangle$. This is understood that the bonding λ_{-} state for H_2 has an admixture of the ionic states H^+H^- and H^-H^+ . This fact will be interpreted further later. To complete the approach we sketch the whole procedure from numerical point of view. First, we take the

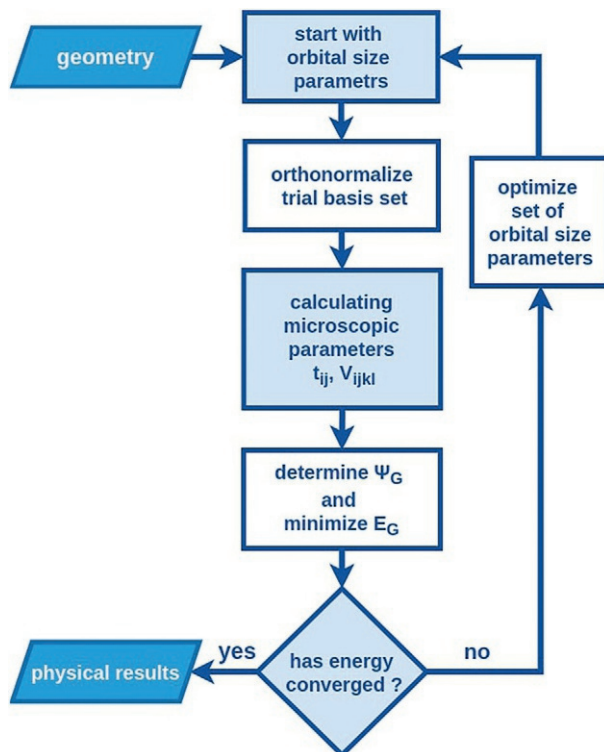


Fig. 2 Flowchart of the EDABI method. The method is initialized by selection of a trial single-particle basis of wave functions (3), and subsequent diagonalization of the many-particle Hamiltonian (6). Optimization of the single-particle-state size leads to an explicit determination of the trial-wave function parameters, microscopic interaction and hopping parameters, as well as ground state energy, and explicit form of the many-particle wave functions (II), all in the correlated interacting state for a given interatomic distance R .

eigenvalue λ_- as our starting point and minimize this energy with respect to the Slater-orbital inverse size α , contained in the assumed functions $\{w_i(\mathbf{r})\}$. This means that we iterate the procedure depicted in Fig. 2 until it converges for optimal $\alpha = \alpha_0$ and for a given interatomic distance. The optimal value of $\alpha = \alpha_0(R)$ is subsequently the same for all the eigenstates $\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5$, and λ_6 . The ground state and the next five excited electron energies (for fixed $R = |\mathbf{R}|$) are exhibited in Fig. 3. Those results are for H_2 molecule; the other examples, LiH and HeH^+ , are discussed briefly later. They are of limited absolute accuracy, but these results are only a starting point to a deeper analysis discussed next.

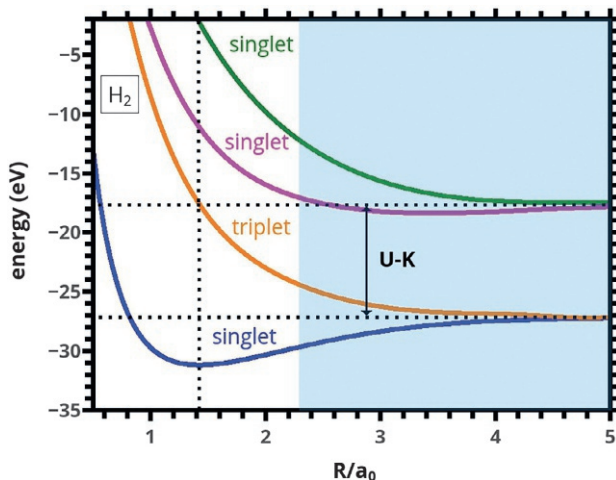


Fig. 3 The lowest energy levels composed of three singlet and three triplet states, with the marked Mott regime and associated with it strong-correlation limit (*shaded area*). The scale $U - K$ represents the effective repulsive Coulomb interaction between electrons, i.e., the HOMO–LUMO splitting. The atomic character of the states shows up gradually becoming atomic with the increasing interatomic distance R .



3. True covalency, ionicity, atomicity: H₂ molecule

3.1 Two-particle wave function and its basic properties—Analytic solution

Further analysis of the bonding requires a calculation of the two-particle wave function in the position (Schrödinger) representation. For that purpose, we quote a general theorem about the N -particle wave function representation in the Fock space (see, e.g., Ref. 16)

$$|\psi_N\rangle = \frac{1}{\sqrt{N!}} \int d^3\mathbf{r}_1 d^3\mathbf{r}_N \psi_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \hat{\psi}_1^\dagger(\mathbf{r}_1) \dots \hat{\psi}_N^\dagger(\mathbf{r}_N) |0\rangle, \quad (12)$$

where $\psi_N(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is the desired wave function for state N in the position representation and $|0\rangle$ represents the vacuum state in the Fock space. We can extract the wave function by reversing the above relation. This leads to the following general explicit expression

$$\psi_\alpha(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \langle 0 | \hat{\psi}_1(\mathbf{r}_1) \dots \hat{\psi}_N(\mathbf{r}_N) | \lambda_\alpha \rangle, \quad (13)$$

where $|\lambda\rangle$ is the eigenstate, for which the wave function ψ_σ is explicitly determined by replacing $|\psi_N\rangle$ with the corresponding Fock-space eigenstate $|\lambda_\alpha\rangle$. For the spin-conserving interaction here, $\sigma \equiv (\sigma_1, \dots, \sigma_N)$ is fixed N -spin configuration. In what follows we discuss the situation for $N = 2$ and $\sigma \equiv (\sigma_1, \sigma_2)$ spin-singlet ground state configuration for the H_2 molecule. Namely, the wave function is obtained by utilizing the expression (2) for the field operators and the anticommutation relations of the creation and annihilation operators, namely

$$\begin{cases} \hat{a}_{i\sigma}\hat{a}_{j\sigma'}^\dagger + \hat{a}_{j\sigma'}\hat{a}_{i\sigma}^\dagger = \delta_{ij}\delta_{\sigma\sigma'}, \\ \hat{a}_{i\sigma}\hat{a}_{j\sigma'} + \hat{a}_{j\sigma'}\hat{a}_{i\sigma} = 0. \end{cases} \quad (14)$$

Additionally, we make use of the vacuum-state property $\hat{a}_{i\sigma}|0\rangle \equiv 0$ for every state $|i\rangle$ (cf. Eq. 7).

In effect, the two-particle wave function representing a single bond in the ground state has the following explicit form

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{2(t + V)}{\sqrt{2D(D - U + K)}} \Psi_{cov}(\mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2} \sqrt{\frac{D - U + K}{2D}} \Psi_{ion}(\mathbf{r}_1, \mathbf{r}_2), \quad (15)$$

where the covalent (Ψ_{cov}) and ionic (Ψ_{ion}) components are

$$\Psi_{cov}(\mathbf{r}_1, \mathbf{r}_2) = [w_1(\mathbf{r}_1)w_2(\mathbf{r}_2) + w_1(\mathbf{r}_2)w_2(\mathbf{r}_1)][\chi_\uparrow(\mathbf{r}_1)\chi_\downarrow(\mathbf{r}_2) - \chi_\downarrow(\mathbf{r}_1)\chi_\uparrow(\mathbf{r}_2)], \quad (16)$$

$$\Psi_{ion}(\mathbf{r}_1, \mathbf{r}_2) = [w_1(\mathbf{r}_1)w_1(\mathbf{r}_2) + w_2(\mathbf{r}_1)w_2(\mathbf{r}_2)][\chi_\uparrow(\mathbf{r}_1)\chi_\downarrow(\mathbf{r}_2) - \chi_\downarrow(\mathbf{r}_1)\chi_\uparrow(\mathbf{r}_2)]. \quad (17)$$

From Eqs. (16) and (17) it is evident that the part (16) represents the covalent (cov) part, whereas (17) represents the combination of the two ionic (ion) configurations of the electrons. Also, note that those wave functions have an involved form; spatially symmetric and spin antisymmetric, as it should be for the spin-singlet state. Parenthetically, these are not single Slater determinant states. Also, their factorization into space and spin parts reflects the fundamental property that they represent separate orbital and internal (spin) symmetries (cf. Ref. 17). The coefficients before the term contain all interactions present in the two-particle single-orbital quantum state. The wave function (15) represents the exact wave function for the HL model, with additional readjustment of orbital size in the resultant (correlated) eigenstate.

In order to interpret the wave function (15) in terms of the original Slater (atomic) wave functions $\psi_i(\mathbf{r}) \equiv \psi(\mathbf{r} - \mathbf{R}_i)$, we make use of transformation (3) and obtain

$$\begin{aligned}\psi_0(\mathbf{r}_1, \mathbf{r}_2) &= (C\beta^2(1 + \gamma^2) - 2\gamma I\beta^2)\phi_{cov}^{at}(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad + (I\beta^2(1 - \gamma^2) - 2\gamma C\beta^2)\phi_{ion}^{at}(\mathbf{r}_1, \mathbf{r}_2) \\ &\equiv \tilde{C}\phi_{cov}^{at} + \tilde{I}\phi_{ion}^{at},\end{aligned}\quad (18)$$

where the two-particle functions $\phi_{cov}^{at}(\mathbf{r}_1, \mathbf{r}_2)$ and $\phi_{ion}^{at}(\mathbf{r}_1, \mathbf{r}_2)$ have the same formal expressions as (16) and (17), respectively, but with molecular functions $\{w_i(\mathbf{r})\}$ being replaced by atomic orbitals $\{\varphi_i(\mathbf{r})\}$. This last expression coincides with the spin-valence bond wave function, except that the postulated coefficients A and (1-A) before the component functions (cf. Fig. 1) are here calculated microscopically. Additionally, as said above, the Slater-orbital size is optimized in the resultant (interacting) ground state. Therefore, one can say that the presented solution exemplifies a direct and exact solution of the original formulation of HL model with subsequent optimization of the initial atomic states. More importantly, the intrinsic covalent bonding (see below) will be defined as a contribution calculated beyond that obtained from HL approach. Achieving these goals is the principal aim of the article so far. Note that the solution in its fully analytic form, but requires the utilization of both first and second quantization (wave and particle) aspects of the problem. In the following subsection, we interpret in detail the obtained results and revise the covalency concept.

3.2 Toward complementary characterization of the chemical bond: The case of H₂ molecule

The wave function (18) reduces to the HL form after taking $\tilde{I} \equiv 0$ and neglecting the spin part, as well as disregarding the readjustment the orbital size in the correlated state. But, most importantly, neglecting to mix the Slater orbitals, i.e., putting in Eq. (3) $\beta \equiv 1$, and $\gamma \equiv 0$. Such an assumption leads to the two-particle wave function (18) in terms of atomic Slater orbitals and without bare covalency (single-particle mixing).¹⁸ This leaves us with the principal question to what extent the factor $\tilde{C}$ in (18) describes the real covalency, as the $\phi_{cov}^{at}(\mathbf{r}_1, \mathbf{r}_2)$ in the original HL approach describes the whole covalency. The fact that it is not the whole story, even when $\gamma \neq 0$, can be demonstrated explicitly by taking $\lim_{R \rightarrow \infty} \gamma_{cov} = \lim_{\gamma \rightarrow 0} \gamma_{cov} = 1$. This is a clearly unphysical result. The reason why it is so is coded in choosing the

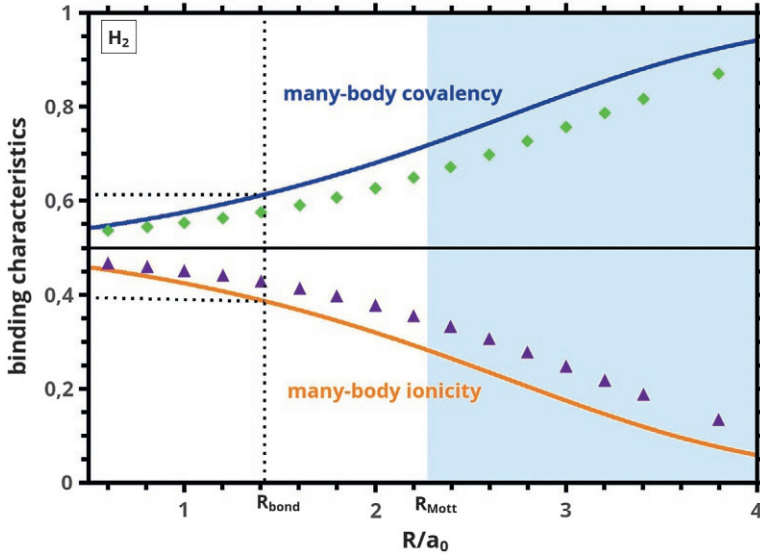


Fig. 4 Two-particle covalency vs corresponding ionicity for H_2 molecule, calculated within EDABI method and compared with the results of Ref. 19. Shaded regime marks a gradual evolution toward *atomicity*, as determined from the Mott–Hubbard criterion (see in the main text). The vertical dotted line marks equilibrium interatomic distance, whereas the horizontal dotted lines illustrate the dominant character of the covalency in that state (with the ratio $r = 1.43 \sim 2 : 1$).

symmetric form of $\psi_{cov}^{at}(\mathbf{r}_1, \mathbf{r}_2)$, which amounts to selecting that function in the form for *indistinguishable* particles, whereas in the limit $R \rightarrow \infty$ the electrons are located on separated atoms and hence are clearly *distinguishable* in the quantum mechanical sense. The unphysical behavior of the covalency factor $\gamma_{cov} \equiv \gamma_{cov}(R)$ is exhibited explicitly in Fig. 4. This behavior is quite astonishing in view of the fact that the same form of postulated (ad hoc) wave function (15) provides a good semiquantitative estimate of the binding energy and the bond length. In retrospect, the definition of covalency in the HL fashion may be expected as insufficient, since it contains as factors the pure atomic functions, which in turn, overestimate the atomicity mixed up with the covalency, as elaborated next.

In order to remove this inconsistency, appearing practically in every approach of selecting the two-particle form based on the indistinguishability of the particles, irrespective of the interatomic distance $\mathbf{R}$, we have the following bold proposal. Namely, to define intrinsic or true covalency we extract from the covalency γ_{cov} in (18) (or, equivalently in (15)) the part γ_{cov} taken in the limit $\gamma = 0$. This is carried out for each R . This step does not

mean that we mix up *indistinguishable* and *distinguishable* states, as it would be principally incorrect. It merely helps to define the *intrinsic covalency* (and degree of *atomicity*) in any nominally covalent system. To summarize, we formally define the true covalency, atomicity, and ionicity for each R as

$$\text{covalency: } \gamma_{cov} \equiv \frac{|\tilde{C}|^2 - |\tilde{A}|^2}{|\tilde{C}|^2 + |\tilde{I}|^2}, \quad (19)$$

$$\text{ionicity: } \gamma_{ion} \equiv \frac{|\tilde{I}|^2}{|\tilde{C}|^2 + |\tilde{I}|^2}, \quad (20)$$

$$\text{atomicity: } \gamma_{at} \equiv \frac{|\tilde{A}|^2}{|\tilde{C}|^2 + |\tilde{I}|^2}. \quad (21)$$

Note that the sum of contributions (two-particle probabilities) is equal to unity. The atomicity is incorporated on the classical level (through the probability).

Next, we incorporate quantitatively the introduced characteristics into the interpretation scheme, but first relate the atomicity to the Mott–Hubbard localization onset, the latter transferred here from the condensed-matter states and adopted to the molecular (finite-size) systems.

3.3 Atomicity as the onset of localization and consistent characterization of the chemical bond

In general, the atomicity here is purposefully associated with the Mott–Hubbard localization, as it provides a physical rationale behind our concept. The localization on parent atoms of electrons in delocalized (band or other) states takes place under a gradually increasing repulsive interaction among the involved particles. In other words, it represents atomization of particles from collective states in lattice systems experiencing an increasing magnitude of repulsive interaction between them. This can be achieved either by increasing the interatomic distance and/or decreasing particle density in the system. In our case here the atomization can be gradual with the increasing interatomic distance. To elucidate how this happens we relate it to the well known Mott²⁰ and Hubbard²¹ criteria for onsets of localized (atomic) behavior of electrons. This is because, we would like to interpret the evolution of molecular H_2 (electron-paired) state into individual singly occupied (atomic) as a gradual process of the Mott–Hubbard localization. Namely, we define the Hubbard and Mott onset criteria adapted to the present situation as

$$\frac{2|t+V|}{U-K} = 1, \text{ or } n_c^{1/d} \alpha^{-1} \equiv \frac{1}{\alpha_0 R_{Mott}} \simeq 0.5, \quad (22)$$

respectively, where α_0^{-1} is the readjusted orbital size at $R = R_{Mott}$ (note, the criteria define, explicitly R_{Mott}). The first of them means that, for $R = R_{Mott}$, the kinetic (hopping) energy, arising from (6) is equal to the interaction energy. That is, for $R < R_{Mott}$ the ratio is greater than unity, whereas for $R > R_{Mott}$ it is smaller than unity and approaches relatively rapidly zero with $R \rightarrow \infty$ (beyond R_{Mott}). Physically, the kinetic energy predominates in the former case; this hopping of electrons, in practice, gets gradually frozen out on atoms as R increases beyond R_{Mott} . On the other hand, the Mott criterion expresses the localization onset when the diameter of the renormalized orbital ($2\alpha_0^{-1}$) crosses the value of interatomic distance; this happens at $R \simeq R_{Mott}$. Quasiclassically, the latter criterion means that the collective electron behavior is established when their orbitals start overlapping strongly.

To visualize this physical and formal reasoning we have plotted in Fig. 5 the left parts of (22) vs R , as well as have marked explicitly their values at

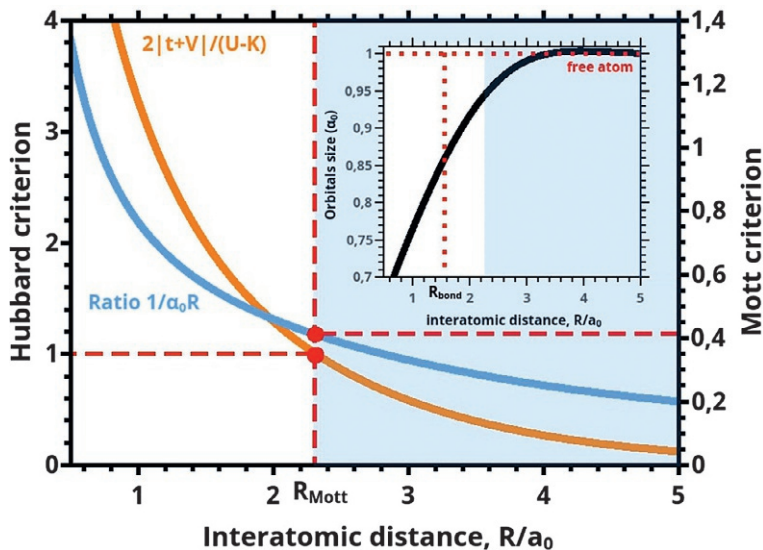


Fig. 5 Hubbard (orange) and Mott (blue) characteristics of atomicity vs interatomic distance R (dashed horizontal lines). The dots mark the points corresponding to Hubbard and Mott criteria. The vertical dotted line marks the onset of Mottness at R_{Mott} . The inset: R dependence of the orbital size of the renormalized atomic wave functions composing the molecular (Wannier) single-particle states. The dotted line marks the equilibrium distance R_{bond} .

$R = R_{Mott}$. The blue shaded area may be called the *Mott regime*. Additionally, in the inset we display the R dependence of the readjusted orbital size α_0^{-1} ; it approaches rapidly the atomic value $a_0 = 0.53 \text{ \AA}$ upon entering the Mott regime. This feature illustrates the rate at which the atomic states are being established with the increasing R beyond R_{Mott} .

The connection of the above criteria with the true covalency (γ_{cov}), atomicity (γ_{at}), and ionicity (γ_{ion}) is shown explicitly in Fig. 6, where the R dependence of those quantities is drawn. Quite remarkably, at $R = R_{Mott}$ the true covalency and atomicity acquire the same value, what illustrates decidedly that the point R_{Mott} expresses a crossover point from covalency to atomicity-dominated regime. In the complementary regime $R \rightarrow 0$, the true covalency and ionicity (atom double occupancy) gradually coalesce. Both figures provide a combined picture in accord with our physical intuition. Simply, the criteria depicted in Figs. 5 and 6 are mutually consistent and complementary to each other. As we concluded in Ref. 11: *This agreement leads to the conclusion that the introduced entities (19)–(21) and (22) are not only relevant in condensed-matter (extended) systems, but also appear as a crucial incipient feature in molecular systems.* Such characterization is possible only with introducing

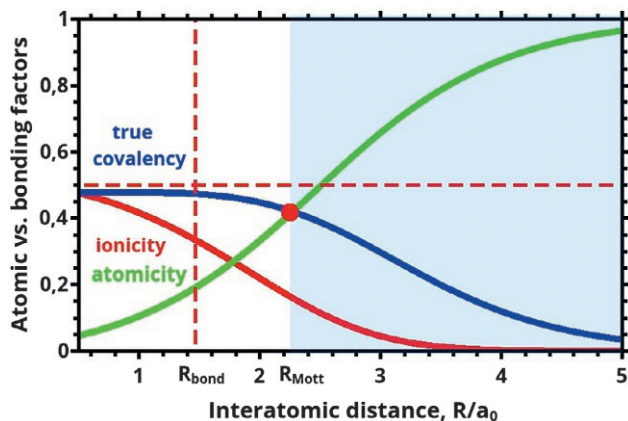


Fig. 6 Intrinsic properties of the chemical bond: atomicity (green), true covalency (blue), and ionicity (red), all as a function of interatomic distance R . They represent the relative weights in the total two-particle wave function. In the $R \rightarrow 0$ limit the atomicity practically disappears and is the only contribution in the separate-atom limit $R \rightarrow \infty$. The solid circle defines the onset of localization effects (*Mottness*) due to interelectronic correlations. If the atomicity is disregarded, the covalency exhibits a drastic nonphysical behavior with increasing $R > R_{bond}$. The figure illustrates a systematic evolution of molecular states into separate atoms and vice versa, formation of molecular states out of separate atoms. The Slater states have a renormalized size $\alpha^{-1} \leq \alpha_B$.

microscopically derived two-particle wave function (15) (or 18) as the proper characteristic of a single bond, which, after all, is composed of electron pair.

We can illustrate further the onset of partial electron localization by calculating directly the density of electrons in the ground state from the formula taken from second quantization scheme, i.e.

$$n_{\sigma}(\mathbf{r}) = \langle \lambda_5 | \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) | \lambda_5 \rangle. \quad (23)$$

Note that $n_{\sigma}(\mathbf{r})$ represents the electron density with spin σ ; it is related to the total particle density by $n(\mathbf{r}) = 2n_{\sigma}(\mathbf{r})$ in the spin-singlet state. This density represents complementary quantity to the probability density $|\psi_0(\mathbf{r}_1, \mathbf{r}_2)|^2$ in the sense that the former represents the physical-particle-occupancy density profile of $n_{\sigma}(\mathbf{r})$ that has been displayed in the panel in Fig. 7 for characteristic interatomic distances $R = R_{bond} = 1.43a_0^{-1}$, $R = R_{Mott} = 2.3a_0^{-1}$, and $R = 4a_0^{-1}$. The parts centered at the nuclei are practically disjoint for $R \gtrsim 4a_0$. For comparison, the results from the valence bond (VB) approach have been also displayed. In both approaches the behavior of the density profiles with the increasing distance is qualitatively similar. The reason is that in both cases the atomicity part has not been excluded. From this point of view, a direct definition (21) of atomicity is the only explicit characteristic.



4. Many-body covalency in related systems

4.1 LiH and HeH⁺

One can apply the same method of approach (EDABI) to other simple molecular systems. In Fig. 8A and B we have plotted the ground state energy vs R for HeH⁺ and LiH and compare it with the results obtained from other methods. As one can see, the results from different methods converge relatively quickly, even before reaching the Mottness (shaded) asymptotic regime. This trend is also observed in the R dependence of the size of orbitals in those two systems, as depicted in Figs. 9A and B. The $1s$ orbital size approaches very rapidly the asymptotic (atomic) limiting value in HeH⁺, whereas the second, $2s$ electron, is responsible for the main part of the bonding with the increasing R beyond R_{bond} . In LiH the situation is different as with the increasing R the atomicity is enhanced and is signaling a robust formation of an almost purely ionic state. Note that the extraction of the atomicity requires a further analysis in this case, as we have to introduce a separate atomicity factor for $1s$ and $2s$ original states. A detailed analysis, as well as the results depicted in Fig. 10 are of numerical character only,

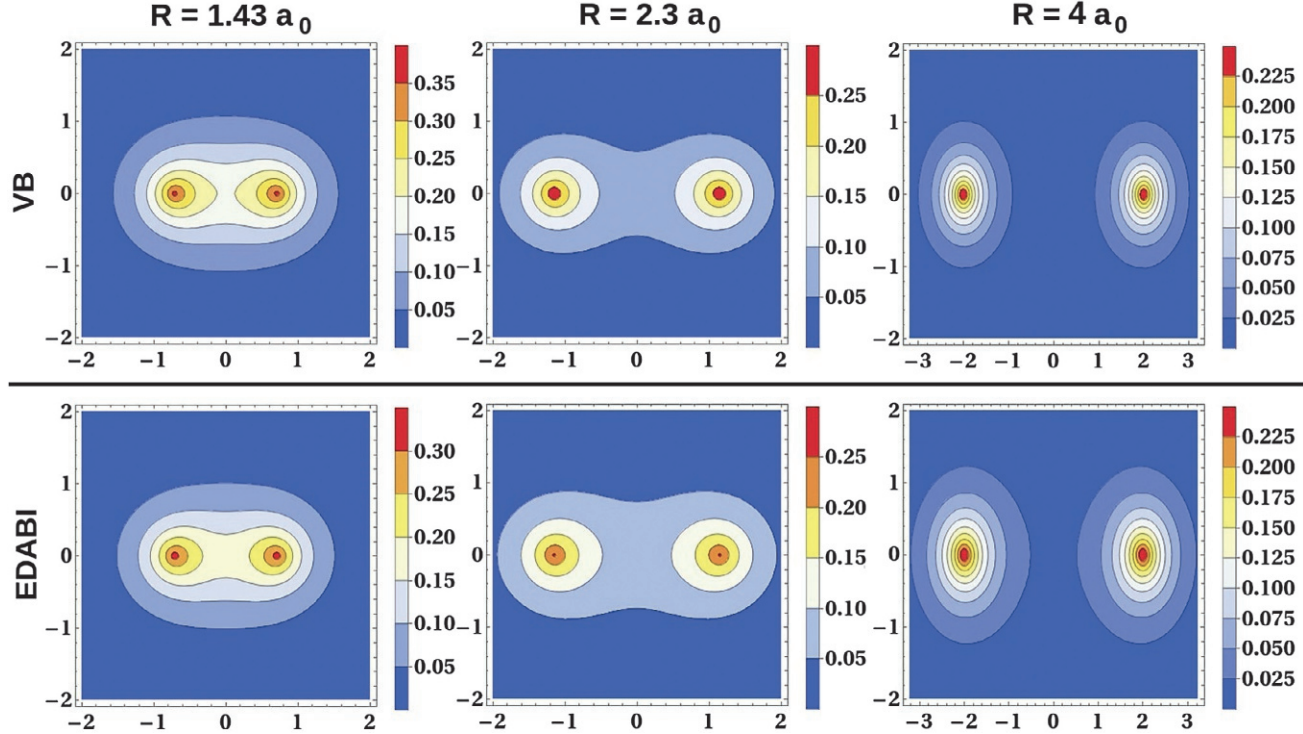


Fig. 7 Electron density $n_e(\mathbf{r})$ for different interatomic distances: $R = 1.43a_0^{-1}$, $R = 2.3a_0^{-1}$, and $R = 4a_0^{-1}$. The parts centered at nuclei are practically disjoint for $R \gtrsim 4a_0$, illustrating the robustness of atomic behavior in that situation. This density contains also the double-occupancy (ionicity) contribution which is becoming rapidly negligible with the increasing R beyond R_{Mott} . The evolution toward the atomic states beyond R_{Mott} is more rapid in the EDABI approach, even so the Heitler–London wave function overestimates the atomicity, as it is composed of bare atomic wave functions.

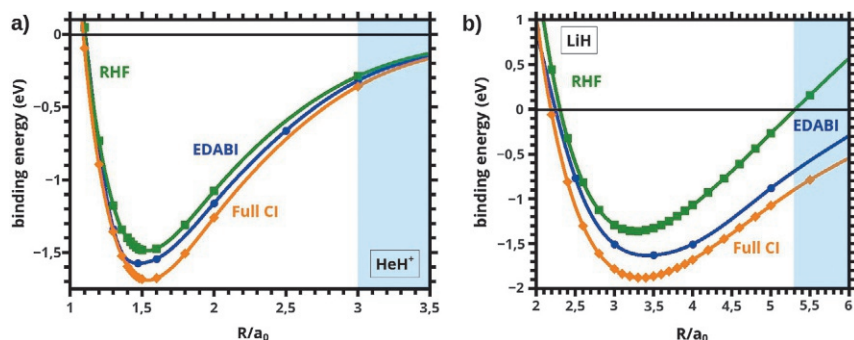


Fig. 8 The HeH^+ and LiH binding energies vs relative interatomic distance, obtained using EDABI method and compared with restricted Hartree–Fock (RHF) and full configuration interaction (full CI) approach taking the minimal basis set for both calculations. $a_0 = 0.53 \text{ \AA}$ is the Bohr radius.

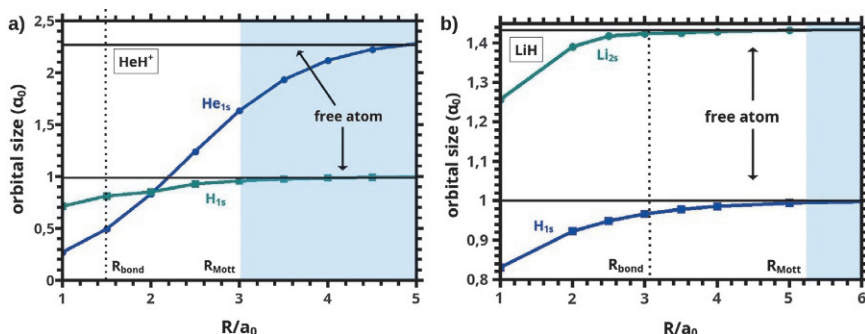


Fig. 9 Renormalized 1s and 2s orbitals size α^{-1} (in Bohr units a_0) vs relative interatomic distance for the H_2 molecule. Note that after crossing the Mott–Hubbard point $R = R_{\text{Mott}}$ α^{-1} approaches rapidly its atomic-limit value $\alpha^{-1} = a_0$.

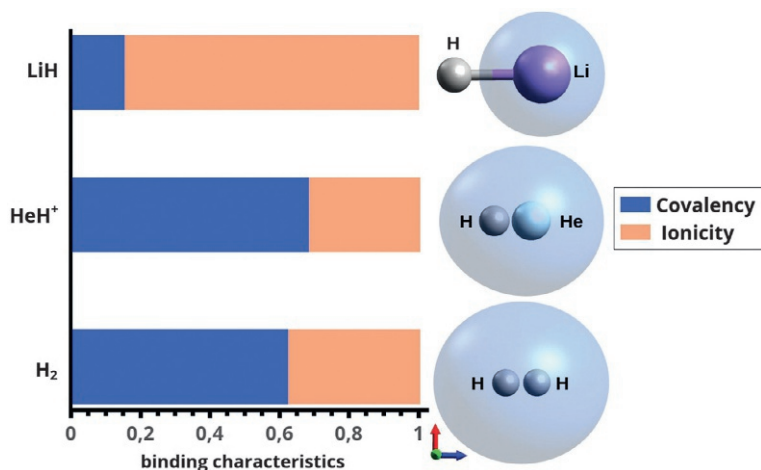


Fig. 10 Illustrative picture of the molecular orbitals (isosurface probability density cut = 0.02) on the right; relative covalency and ionicity contributions, without the atomicity extracted, on the left.

as in this case with two different orbitals an analytic discussion is not possible [e.g., we should use the full matrix form of (9)]. To summarize, the related molecular systems such as those discussed briefly above, require a further analysis to extract the atomicity in heterogeneous systems, independently of the degree of covalency in the physical ground state. This statement is illustrated in Fig. 10 with the starting degree of covalency/ionicity for those systems considered. Additionally, the values of calculated microscopic parameters of Hamiltonian (6), as well as of other microscopic characteristics, are provided in our original papers^{10,11} (see section *Supporting Information* in Ref. 11).

4.2 Essential extension: The hydrogen bond—An outline

Recently, application of a similar model based on the second quantization representation to description of the hydrogen bond has been formulated.^{22–26}

In that model the resonating fermion is proton and is taking between two more complex molecules. In particular, the question of defining covalency in that case has been raised.^{27–29} Simply speaking, the proton hops between two (in)equivalent positions, in an analogical situation to that for electrons between two protons in H_2 molecule. In the simplest picture of such a hydrogen bond one has the situation with quantum tunneling of a proton regarded now as a quantum particle between two positions with energy ϵ_1 and ϵ_2 , created by two larger donor/acceptor groups X_1 and X_2 as shown in Fig. 11. If we ignore the explicit electron charge-density shift in X_1 and X_2 , associated with the proton hopping, then the proton between the two positions labeled with ϵ_1 and ϵ_2 can be modeled by Hamiltonian

$$\hat{\mathcal{H}} = \epsilon_1 \hat{a}_1^\dagger \hat{a}_1 + \epsilon_2 \hat{a}_2^\dagger \hat{a}_2 + t \left(\hat{a}_1^\dagger \hat{a}_2 + \hat{a}_2^\dagger \hat{a}_1 \right) \quad (24)$$

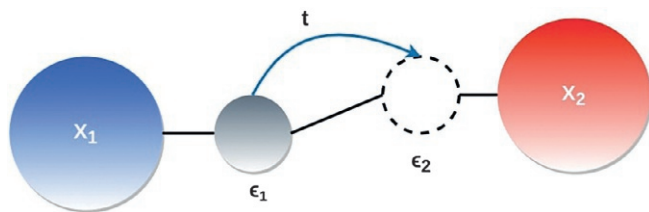


Fig. 11 Schematic representation of proton resonant hopping of magnitude t , as the simplest model of hydrogen bond. X_1 and X_2 symbolize donor and acceptor molecules. Different reference orbital energies ϵ_1 and ϵ_2 refer to two possible proton positions.

where t is the hopping and $\hat{a}_i^\dagger(\hat{a}_i)$ is spinless proton creation (annihilation) operator at site ϵ_i . The energy shift $|\epsilon_1 - \epsilon_2| \neq 0$ appears as the proton hops between the two sites. This simple two-site model leads to bonding and antibonding states of the form

$$x_{1,2} = \frac{1}{2} \left[(\epsilon_1 + \epsilon_2) \mp \sqrt{(\epsilon_1 - \epsilon_2)^2 + 4t^2} \right]. \quad (25)$$

The eigenenergies are degenerate with respect to proton spin direction. Those energies are depicted as a function of $\Delta\epsilon \equiv \epsilon_1 - \epsilon_2$ in Fig. 12 for different t values. Such a simple model provides the bonding-antibonding. The corresponding eigenfunctions can be obtained easily will not be reproduced here.

The more realistic situation is drawn in Fig. 13 for the adenine–thymine exemplary case. In this situation there are two hydrogen bonds as shown, as well as two proton transfers. The resultant schematic model is drawn at the bottom, where now both the protons spins and transverse (vertical) hopping processes $\sim t'$ have been marked. This bottom part leads to the model with two fermions (protons) in 4-site system. It leads to $\binom{8}{2} = 24$ spin-singlet and -triplet states. The Hamiltonian is of the form similar to expression (6), which can be analyzed formally rigorously. We omit here a detailed examination of the resultant states. This example is to show only that

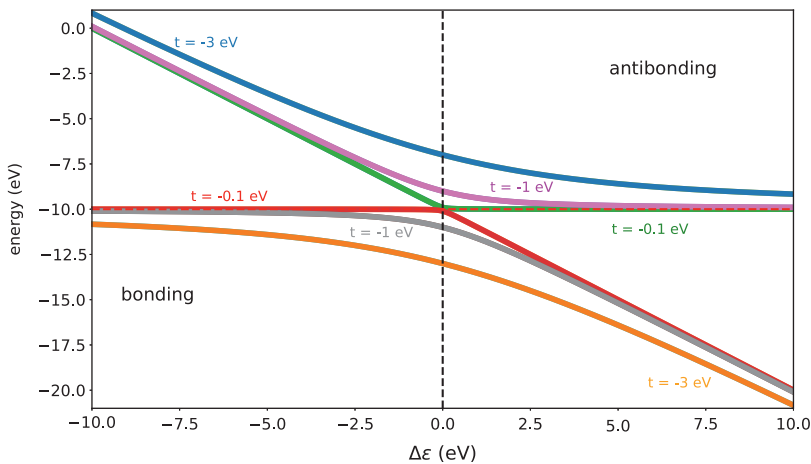


Fig. 12 Bonding and antibonding states for resonating fermion (proton) between two sites as a function of the atomic energy difference. Three values of the hopping t have been selected.

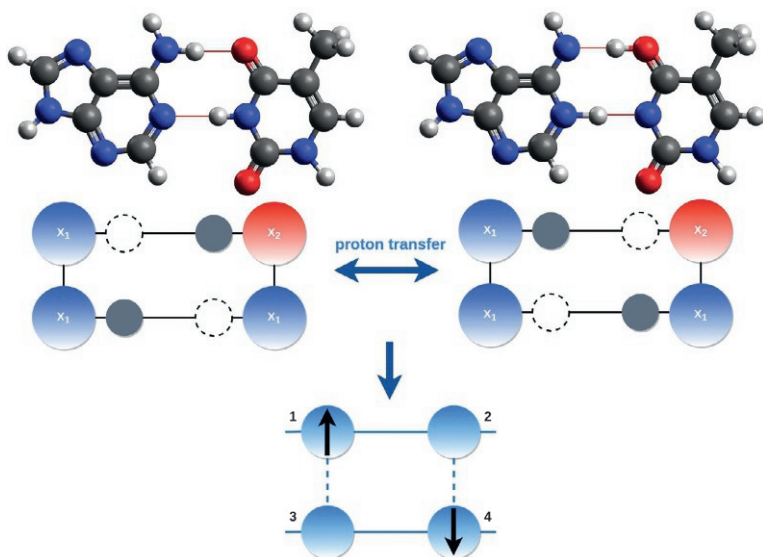


Fig. 13 *Top row:* Two resonating proton configuration before (*left*) and after correlated pair hopping. Adenine (A) and thymine (T) pair has been selected. *Middle row:* Schematic representation of the processes depicted in the top row. *Bottom row:* 4-site model with two protons with their resonating between the sites. *Dashed vertical lines* represent virtual hopping between the rungs. An inclusion of the electron density shift may be included by vertical hops of the electrons toward the hopping proton.

the model constructed for simple molecules can be readily constructed and adopted also to more involved situations. Namely, the hopping of the proton to the particular site can be associated with a motion of charge compensating electron toward the incoming proton to the closest site, i.e., the vertical electron hopping toward the proton (hopping of two electrons in total, in opposite direction, to that of each of the proton). Such a simple model

requires determination of $\binom{4}{2}^4 = 1296$ -fermion states. In essence, the double hydrogen bond in that case is composed of both the intersite proton resonance of a covalent type and associated with it electrostatic attraction of electron to the hopping proton in its final state. We should see a progress along this lines in near future.



5. Outlook

In this chapter we have analyzed in detail the nature of covalency and have elaborated on it by defining an *intrinsic (true) covalency*, in addition to

ionicity, as well as have defined the degree of *atomicity* in nominally covalent state. With introduction of the atomicity we have defined a degree of atomic character in the resultant bound state. Our analysis starts with the exact solution of the HL model of bonding in H_2 molecule as well as extends it. The analyzed solution and bonding properties are carried out explicitly and this possible by starting from the analytic solution of the model. This solution, in the closed form, is in turn, possible with the help of our original EDABI approach.

The method detailed for the H_2 -molecule complementary characterization can also be applied to other simple molecular systems such as LiH and HeH^+ , each discussed briefly. Additionally, a similar modeling can also be carried out for the analysis of hydrogen bond, as briefly outlined at the end. We should be able to see an important progress in understanding these systems along these lines in the near future.

Acknowledgments

This work was supported by Grants OPUS No. UMO-2018/29/B/ST3/02646 and No. UMO-2021/41/B/ST3/04070 from Narodowe Centrum Nauki. We thank our colleagues from the Chemistry Department of the Jagiellonian University for numerous discussions and general remarks during the course of this project.

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Further reading

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Exact Entanglement correlation complements the chemical bond description

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We analyze the properties of the exact solution obtained by us recently for the extended Heter-London model for chemical bonding which has an analytic form. The emphasis is put on defining two-particle entanglement correlation as the complementary characterization of the chemical bond and relating it to the partial atomicity and the so-called true covalency. The newly introduced characteristics remove the deficiency of the standard definition of covalency which now vanishes in the limit of the separated atoms. In effect, a gradual evolution of the system of two indistinguishable electrons in a bound state into their distinguishable correspondents can be traced systematically. The present analysis has a universal meaning and may also be applied to more complex systems.

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A fully quantitative understanding of the nature of the covalent bond is fundamentally important for describing various chemical, physical, and biological systems. In the canonical case of the H_2 molecule, the bond is depicted as a quantum mechanical bound state of two hydrogen atoms in the spin-singlet configuration of two electrons, minimally affected by the proton nuclear spins. Heitler and London established the initial quantitative description of the H_2 molecule [1] within the essentially single-particle (Hartree-Fock) approximation of the two-electron state. This approach still serves as the foundation for a more comprehensive description, incorporating the mixing of virtually excited states of the constituent electrons [2].

Recently, we have rigorously solved the extended Heitler-London model, accounting for all-electron interactions in the ground state of the two-particle system with the inclusion of the $1s$ -orbital contraction contained in the resulting covalent and ionic parts of the total wave function [3]. A crucial feature of this exact solution is the derivation of the precise and analytic form of the two-particle wave function. This enabled a redefinition of the bond covalency and ionicity, along with the introduction of the degree of atomicity persistent upon bond formation, which in turn opens up a new path to a complementary bond characterization.

Here we demonstrate that the previously defined *true covalency* [4–6], based on the ideas of the Mott-Hubbard localization, can be quantitatively related to the von Neumann entropy for the interacting and entangled two-electron states. Essentially, we name this entropy as *the entanglement correlation* between the true covalent and ionic counterparts, thus complementing each other in the quantum mechanical manner. From this perspective, our findings complete the energy-based quantum mechanical description of the covalent bond, here exemplified for the homopolar molecule H_2 . Moreover, our approach resolves the unphysical feature, observed in both the Heitler-London and the succeeding papers, for which the covalency increases with the increasing interatomic distance [7]. Such a refined analysis can be carried out in a physically clear way only by introducing the density matrix formulation with the admixture of atomicity to the pure bonding state. Finally, the quantum information point of view analysis provides us with an insight into the bond evolution with the interatomic distance R gradually approaching the dissociation limit, $R \rightarrow \infty$, when the bonding electrons are getting localized on the parent atoms and thus become *distinguishable in the quantum mechanical sense*.

THEORY. We start with the expression for the two-particle wave function in the spin-singlet ground state, here rewritten in the second-quantized form [4]

$$\begin{aligned}
 |\Psi_G\rangle &= \frac{2(t+V)}{\sqrt{2D(D-U+K)}} \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger - \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle \\
 &\quad - \frac{1}{2} \sqrt{\frac{D-U+K}{2D}} \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle \\
 &\equiv C\psi_{cov}(\mathbf{r}_1, \mathbf{r}_2) + I\psi_{ion}(\mathbf{r}_1, \mathbf{r}_2)
 \end{aligned} \tag{1}$$

where the first and second terms describe the covalent and ionic parts, respectively. The coefficients represent: t and V are the hopping and correlated hopping integrals, U and K are the magnitudes of the intraatomic and interatomic Coulomb repulsion, and $D \equiv \sqrt{(U-K)^2 + 16(t+V)^2}$. The creation operator part represents the intersite (first term) and intrasite spin singlet parts. They reflect microscopic parameters of the Hamiltonian [4, 5] and are calculated microscopically within the EDABI procedure (see Methods). The representation Eq. (1) is written in the basis of molecular wave functions. For the purpose of subsequent analysis we need a representation of Eq. (1) in terms of single-particle Slater-atomic basis. Its explicit form is

$$\begin{aligned}
 |\Psi_G\rangle &\equiv (C\beta^2(1+\gamma^2) - 2\gamma I\beta^2) |\phi_{cov}^{at}\rangle \\
 &\quad + (I\beta^2(1-\gamma^2) - 2\gamma C\beta^2) |\phi_{ion}^{at}\rangle \\
 &\equiv \tilde{C} |\phi_{cov}^{at}\rangle + \tilde{I} |\phi_{ion}^{at}\rangle
 \end{aligned} \tag{2}$$

where the sum $C^2 + I^2$, as well as $\tilde{C}^2 + \tilde{I}^2$, should be both normalized to unity and their explicit form has been rigorously determined previously [4, 5]. The physical meaning of the consecutive terms is the same as above. For the purpose of the present analysis, we write those components again in the explicit second-quantized form. Parenthetically, if we disregard the kets in Eq. (1) the resulting entities represent the corresponding wave functions in the Schrödinger position representation.

One important side remark should be made at this point. Namely, when plotting the covalent and ionic coefficients with increasing interatomic distance R , then the covalency ($\gamma_{cov} \equiv C^2/(C^2 + I^2)$) also increases and reaches its maximal value of unity in the $R \rightarrow \infty$

limit. This is an unphysical result and calls for a revision of the covalency definition in this form. To define *the true covalency* ($\gamma_{cov} \equiv (\tilde{C}^2 - \tilde{A}^2)/(\tilde{C}^2 + \tilde{I}^2)$) we have introduced the atomic coefficient ($\tilde{A} \equiv C\beta^2$) and atomicity $\gamma_{at} \equiv \tilde{A}^2/(\tilde{C}^2 + \tilde{I}^2)$ have subtracted the latter and then obtain the proper physical behavior of the quantities in the dissociation limit: $\gamma_{cov} \rightarrow 0$, $\gamma_{ion} \rightarrow 0$, and $\gamma_{at} \rightarrow 1$ [4, 5].

By invoking the atomicity and hence defining the true covalency we introduced a mixed-state ingredient in the so-far pure-state quantum mechanical analysis. Therefore, to select a proper language for this new situation, we turn to the appropriate density matrix description. Intuitively, it amounts to replacing the covalent factor with its true covalency correspondent. Explicitly, as evident from Eq. (1) we can define the two-particle density matrix in the form of 4×4 matrix with the following trial states $|\uparrow_1\downarrow_2\rangle$, $|\downarrow_1\uparrow_2\rangle$, $|\uparrow_1\downarrow_1\rangle$, and $|\downarrow_2\uparrow_2\rangle$ (where the subscripts 1 and 2 label the component atoms) from which all the spin-singlet states are composed of. In effect, the density matrix takes the starting form

$$\rho = \frac{1}{C^2 + I^2} \begin{pmatrix} C^2 & 0 & IC & 0 \\ 0 & C^2 & 0 & IC \\ IC & 0 & I^2 & 0 \\ 0 & IC & 0 & I^2 \end{pmatrix} \quad (3)$$

Next, we subtract atomicity $\tilde{A}$ from the above C factor in this expression. Then, the von Neumann entropy for this mixed state is determined in the following way

$$S \equiv -Tr(\rho \ln \rho) = -2(\gamma_{cov} + \gamma_{ion}) \ln(\gamma_{cov} + \gamma_{ion}) = -2\gamma_{bond} \ln(\gamma_{bond}). \quad (4)$$

We are now ready to discuss the results and relate the bonding factors to the von Neumann entropy, which will allow us to interpret the latter as expressing the *entanglement correlation*.

RESULTS. To illustrate the evolution of the bound state we have plotted in Fig. 1 a-d electron density profiles, drawn on (x, y) plane and at two interatomic distances: at equilibrium distance $R = R_{eq} = 1.43a_0$ and the Mott-Hubbard threshold (when the kinetic-energy and interaction magnitudes are equal) $R = R_{Mott} = 2.3a_0$ [4, 5]. The actual densities are shown in Fig. 1(a) and (d), whereas the red parts in (b) and (e) mark the atomic- and ionic-part contributions, while the blue parts mark the total electron density. Furthermore,

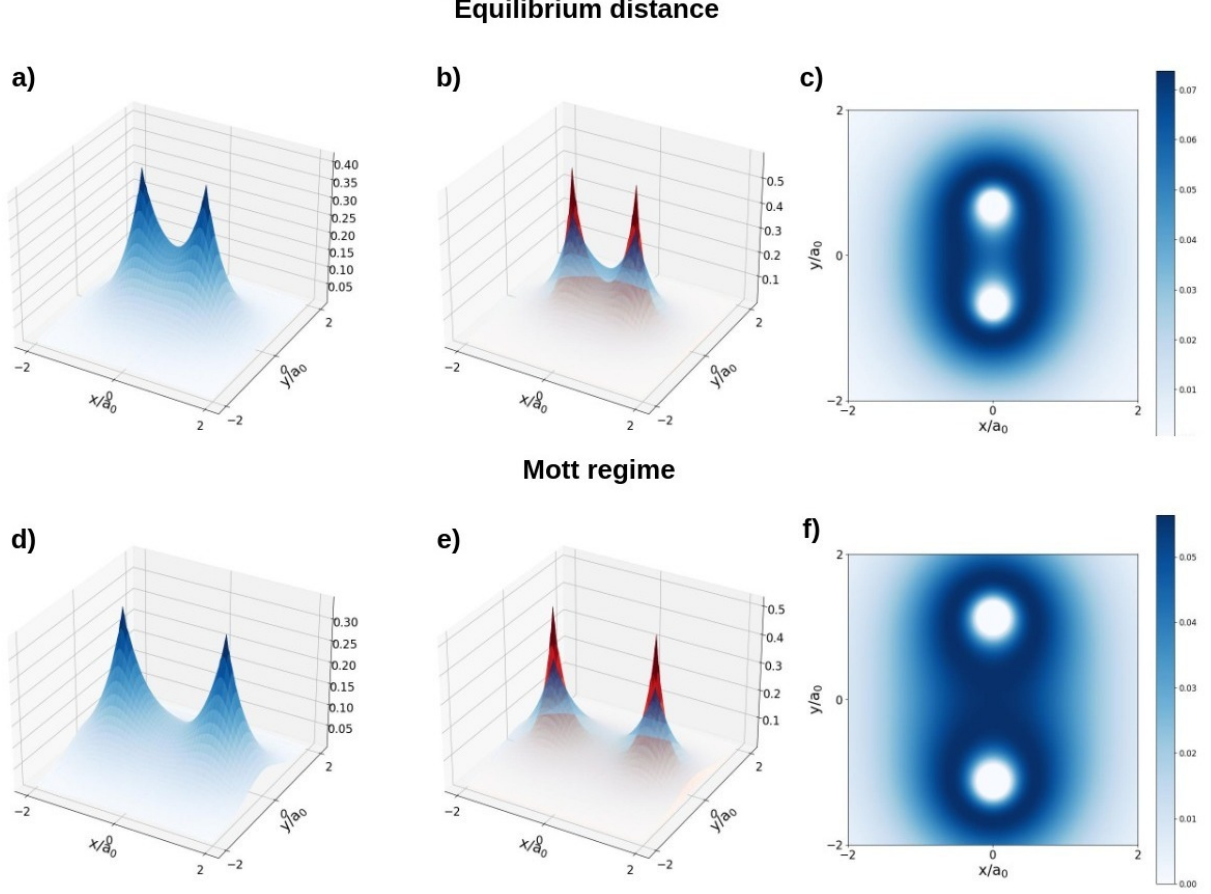


FIG. 1: Left: Electron density profiles for two interatomic distances (equilibrium distance $R_{eq} = 1.43a_0$ and Mott-Hubbard boundary $R_{Mott} = 2.3a_0$) specified. Right: The purely covalent part of the wave function with the atomic and admixed ionic-covalent part subtracted. Note that the bonding is nonlocal and therefore requires a nonlocal (global characteristic): this is provided by either γ_{cov} or $\gamma_{cov} + \gamma_{ion}$ or by the von Neumann entropy, as discussed in detail in the main text.

Figs. (c) and (d) illustrate the corresponding densities on the plane $z = 0$ with both the atomic part and the ionic-covalent admixture subtracted. From the two last profiles, one can see that the covalent bonding encompasses the space in between the two proton positions, which is not limited only to the region along the line connecting them, as one would presume intuitively, so although its overall magnitude is quite small.

In Fig. 2 we present the von Neumann entropy *versus* the bonding factor, $\gamma_{cov} + \gamma_{ion}$ with characteristic points marked. On the upper scale the corresponding interatomic distances are labelled. The most important feature of this diagram is that the maximal entropy appears in neighborhood of the point where the kinetic energy and the interaction parts are comparable, i.e., close to the Mott-Hubbard (M-H) crossover point. The whole interaction-

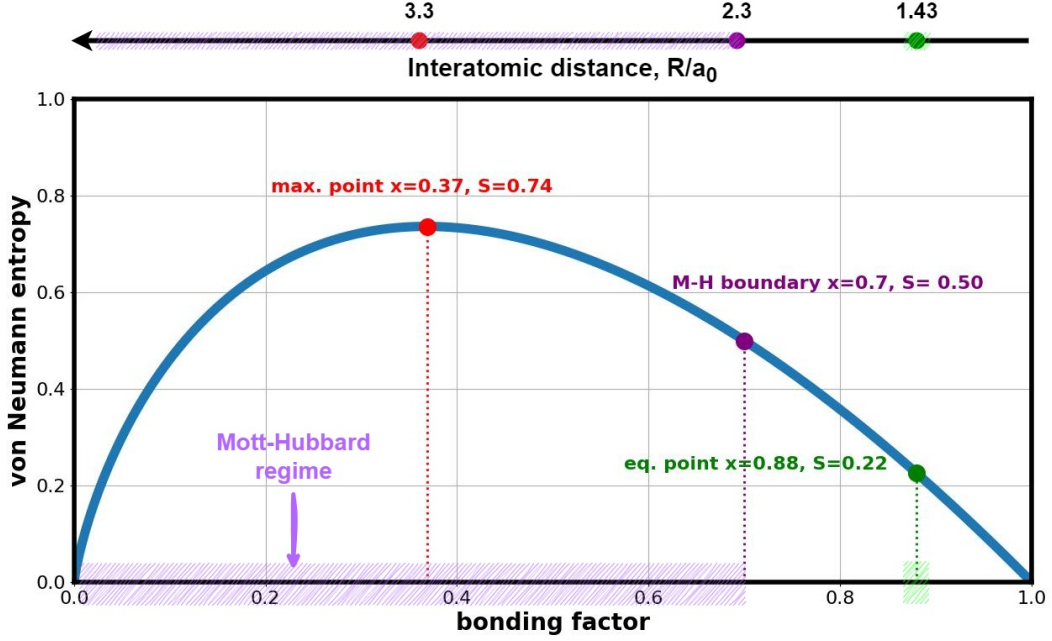


FIG. 2: The von Neumann entropy as a function of bonding factor, $\gamma_{cov} + \gamma_{ion}$. The characteristic points are specified. The upper scale marks characteristic interatomic distances. The purple hatched area corresponds to the Mott-Hubbard regime, emphasizing the region where electronic correlations are predominant.

dominated M-H regime is also marked. Because of those features, we can call the entropy as the exponent of the *entanglement correlations*. Note also that the entropy vanishes in the $R = 0$ and ∞ limits, as we consider the dynamics only in the spin-singlet subspace of the total Fock space. The entanglement expresses the mutual correlation between the covalent and ionic parts induced by the competition part and the localization tendency induced by strong repulsive Coulomb interaction. The latter is responsible for the emergent atomicity.

The bonding features introduced by us as a complementary characterization to the standard energy considerations (see below) are summarized in Fig. 3, all as a function of the interatomic distance. Explicitly, as said above, the point of maximal entanglement correlation is close to that, where the bonding $\gamma_{cov} + \gamma_{ion}$ and atomicity coincide. The latter may be regarded as a critical point for the crossover trend from the dominant single-particle bonding (characterized by the kinetic energy associated with the electron hopping) to the interaction-dominated (M-H) regime. The point is relatively far away from the equilibrium distance R_{eq} but may play a crucial role in the molecule dissociation process under the presence of a

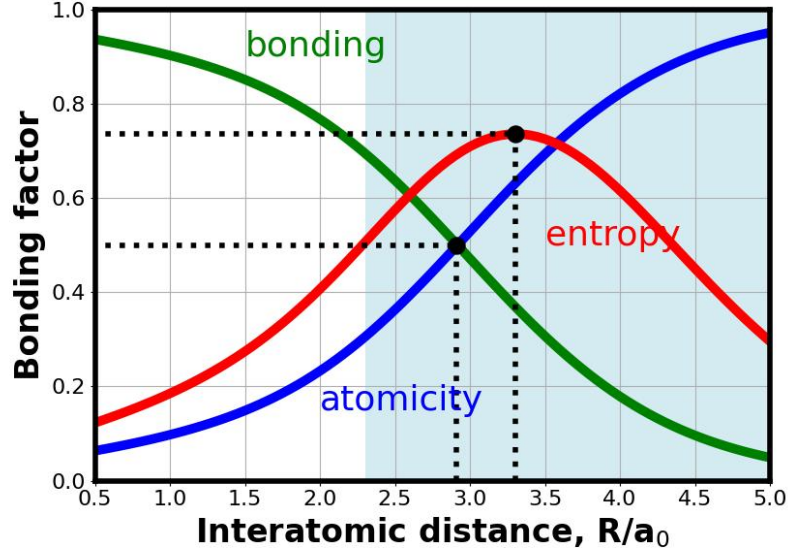


FIG. 3: Relation between the bonding factor, atomicity and entanglement correlation (von Neumann entropy) as a function of interatomic distance. The shaded blue area corresponds to the Mott-Hubbard (crossover) regime [4, 5].

catalyst. To summarize the meaning of Figs. 2 and 3, they represent a fully complementary quantum characterization of the single chemical bond in the two-atomic molecules such as H_2 and related systems [3]. Nonetheless, the homopolar H_2 case represents the clearest situation as the atoms are the same and hence the quantum evolution with R , not distributed by extrinsic factors such as the component atoms inequivalence.

RELATED ENERGY CHARACTERISTICS. Above we have connected directly the single-particle *versus* interaction energy competition to the entanglement entropy related to it. As our method of approach allows for a detailed decomposition of the total bonding processes into various energy contributions, we now discuss on the evolution of the latter with the interatomic distance. In this manner, a comparison with a more standard approach can be made [8]. For that purpose, we plot in Fig. 4 the bar charts of those terms composing the total ground state energy (per atom): hopping ($2|t| \langle \hat{a}_{1\sigma}^\dagger \hat{a}_{2\sigma} \rangle$), intraatomic Coulomb interaction ($U \langle \hat{n}_{1\uparrow} \hat{n}_{1\downarrow} \rangle$) and interatomic ($\frac{1}{2}K \langle \hat{n}_1 \hat{n}_2 \rangle$) Coulomb repulsion terms, and hopping correlation ($2V \langle \hat{n}_{1\uparrow} \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\downarrow} \rangle$) terms (the Heisenberg exchange term $\sim J$ has been ignored as it does not appear in the bonding factors). It follows that between $R = R_{eq}$ and $R = R_{Mott}$ the total hopping ($\sim 2|t + V|$) and the effective Coulomb interaction ($\sim U - K$) terms are of comparable magnitude; this circumstance reflects the Hubbard criterion that $(2|t + V|)/(U -$

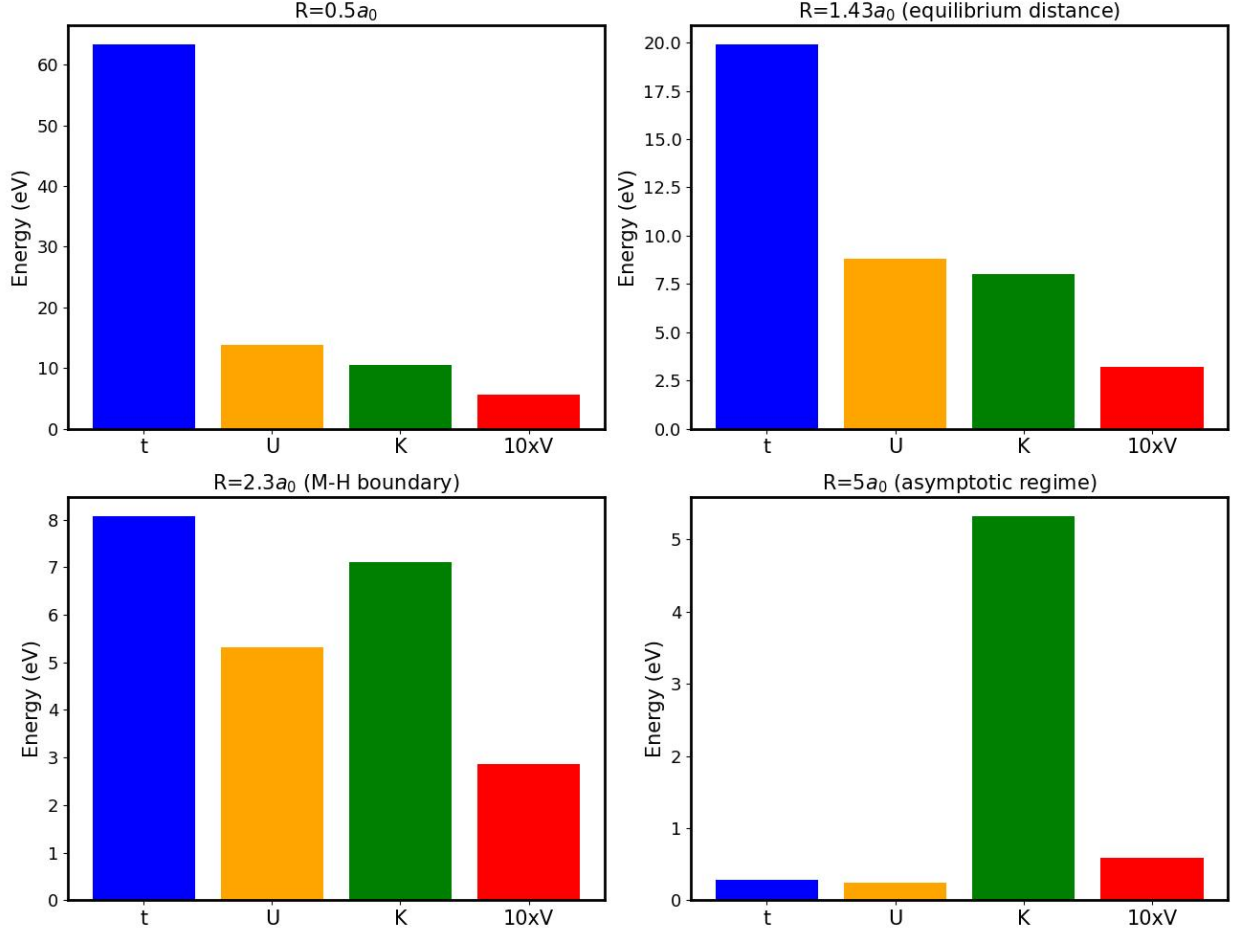


FIG. 4: The bar charts specifying the relative energy contributions to the total energy of different components for four interatomic distance values ($1a_0$, equilibrium distance $1.43a_0$, Mott-Hubbard criterion $2.3a_0$, and $5a_0$). The Heisenberg exchange integral is not accounted for in the wave function coefficients and is disregarded here.

$K)) \simeq 1$ then. Parenthetically, as elaborated earlier [4, 5] the criterion is the fundamental formal reference point of the whole analysis of atomicity. In effect, we cannot say whether the kinetic energy always represents the signature of the bonding. Instead, the factors displayed in Fig. 5 can be together unequivocally assigned as such. This conclusion can be illustrated further by calculating the dynamic correlations attached to the above terms. Namely, for example the orbital part $\langle \hat{n}_1 \rangle + \langle \hat{n}_2 \rangle = 2$, hopping probability $\langle \hat{a}_{1\sigma}^\dagger \hat{a}_{2\sigma} \rangle = 16|CI|$, intrasite Coulomb correlation $\langle \hat{n}_{1\uparrow} \hat{n}_{1\downarrow} \rangle = 4C^2$, intersite Coulomb correlation $\langle \hat{n}_1 \hat{n}_2 \rangle = 2I^2$, exchange spin correlation for the singlet state is obviously equal to unity, correlated-hopping correlation $\langle \hat{n}_{1\uparrow} \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\downarrow} \rangle = 16|CI|$. In this manner, we relate directly the dynamic correlations to the bonding characteristics. This very important side conclusion could be also elaborated

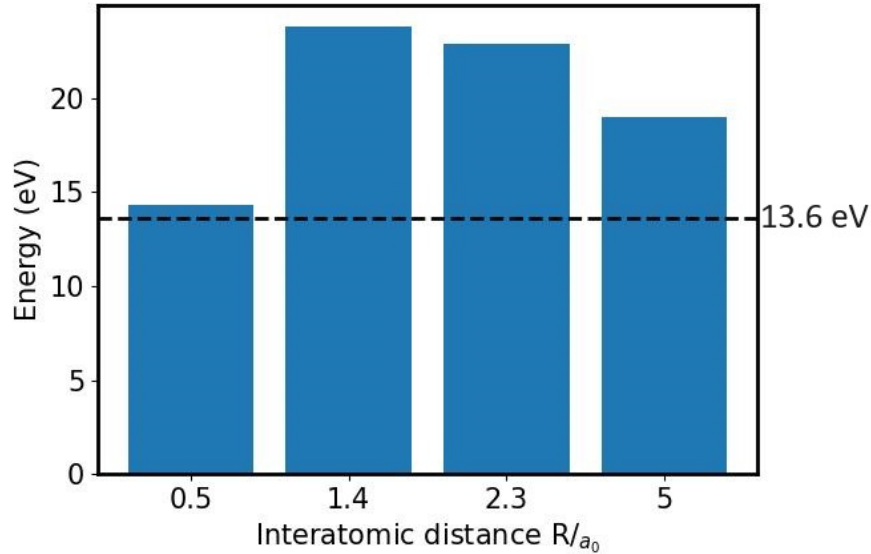


FIG. 5: The adjusted atomic (ϵ_{at}) dynamic contribution to the energy for H_2 molecule with readjusted atomic orbital size for the specified interatomic distances R . The enhancement above reflects the orbital size contraction. The atomic energy is largely compensated by the intersite Coulomb interaction.

for heteropolar systems such as LiH , HeH^+ , etc., where the atomic energy part shifts the balance toward enhanced ionicity and atomicity. In the end, we should note that even the atomic part of the energy varies substantially with increasing R , as illustrated in Fig. 5. We see that this energy (on an absolute scale) is enhanced in the molecular state with respect to the value of R it would be in the limit of separated atoms (cf. dashed red line). The latest property provides an additional rationale for subtracting the atomic part in Figs. 1 (c) and (f) when explaining the meaning of the true covalency.

METHOD. Our approach is based on the method EDABI (**Exact Diagonalization Ab Initio**) proposed earlier for nanosystems with correlated electrons [4, 5]. We start with the assumption of the trial single-particle wave function basis which defines a truncated Hilbert-Fock space, in which a complete Hamiltonian in the second quantization representation is determined. The truncated basis is composed of both molecular (Mulliken-Wannier) states $w_{i\sigma}(\mathbf{r}) \equiv w_{\sigma}(\mathbf{r} - \mathbf{R}_i)$, $i = 1, 2$ is formed in terms of which the microscopic parameters of the Hamiltonian $\hat{\mathcal{H}}$ in the Fock space are determined. The Wannier states are composed as a superposition of atomic Slater states with their size (determined analytically) the inter-correlated state (eigenstates of $\hat{\mathcal{H}}$). The lowest eigenstate is one of the three $^1\Sigma_g^+$ ground

states representing the ground state. The remaining five eigenstates (two singlets and three triplets) are the excited states. Finally, the two-particle wave function in an analytic form is determined by the transformation of the eigenvector in terms of the Fock space back to the Hilbert space [9]. The two-particle wave functions are determined analytically and for each of them, the crucial physical properties are discussed elsewhere [MH & JS, in preparation].

OUTLOOK. We reiterate that the molecular state, analyzed here within the exact solution of the extended Heter-London model, presents itself as a distinct case of the entanglement evolution when compared to that of noninteracting bosons [10]. This is because here the particles interact and for interatomic distance $R \rightarrow \infty$ gradually become disentangled but still bound to the parent atoms, i.e., *distinguishable* in the quantum-mechanical sense [11]. In this respect the *indistinguishability* $\rightarrow$ *distinguishability* transformation is quite analogous to that of delocalization-localization (Mott-Hubbard) transition in condensed multiparticle systems [12–14]. Here the transformation is gradual but still conveys the same physics as the supercritical delocalization-localization behavior in the other nanosystems [15]. In effect, it brings this aspect of Mott phenomenon to the molecular level. In effect, a degree of quantum statistical behavior may be implemented into the pure quantum-mechanical analysis of those systems. Obviously, the analysis of more involved and heterogeneous systems (e.g. LiH, HeH⁺, H₂⁺ etc.) may contribute to the possibility of modifying the particle indistinguishability and analyze resulting specific emergent potentially atomic behavior.

One may also raise the question of how the behavior beyond the standard equilibrium configuration ($R = R_{eq}$) of molecules (e.g. H₂) can be made accessible for studying the most interesting situation with $R \gtrsim R_{Mott}$. One can think of screening the Coulomb interaction by invoking either its reduction by a medium or a proper catalyst. But then, one must be very careful and do not change the component particles' indistinguishability. Finally, the physics of, e.g., H₂ molecule beyond $R = R_{eq}$ may be useful in enhancing its reactivity.

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Role of Kinetic Exchange and Coulomb Interaction in Bonding of Hydrogen Molecular Systems and Excited States

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We present a detailed investigation of the electronic structure and bonding characteristics of hydrogen-based molecular systems (H_2^+ , H_2 , H_2^-) using the Exact Diagonalization Ab Initio (EDABI) approach within the framework of combined first- and second-quantization. By analyzing the relative contributions of kinetic exchange and effective Coulomb interactions, we provide a comprehensive understanding of covalency, atomicity, and ionicity as a function of interatomic distances. Our approach leverages exact solutions of the extended Heitler-London model to quantify these interactions, extending the analysis to the discussion of properties of excited states and the dissociation limit to these molecules. The findings reveal significant differences in bonding characteristics, particularly highlighting the stability and bonding nature of the neutral H_2 molecule compared to its ionic counterparts. This study not only enhances an understanding of molecular interactions in hydrogen systems but also demonstrates the potential of the EDABI approach in developing more accurate computational models in quantum chemistry.

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Fundamental understanding of molecular electronic structure and bonding is crucial for various applications in chemistry and physics. Despite numerous remarkable works published, the discussion on selected aspects of chemical bonding remains intense, even for relatively simple systems like diatomic molecules [1]. In our view, this ongoing debate is related to the advancement of numerical methods, which remain interpretative challenges despite achieving highly accurate numerical results with the appropriate level of complexity and sophistication.

To provide a brief outline of this discussion, it is worth mentioning works related to the ambiguity of the concepts of ionicity and covalency in chemical bonds [2, 3], as well as attempts to explain the covalency of the bond in the hydrogen molecule and other diatomic molecules [1, 4–6]. Our contribution to this discussion has been to provide the complementary characteristics of the chemical bond such as the atomicity and true covalency [7, 8] or our newest paper about entanglement correlations as the alternative bonding characteristic [9].

In this paper, we use the EDABI approach to investigate the detailed electronic structure of hydrogen-based molecular systems, specifically H_2^+ , H_2 , and H_2^- . We employ the formalism of second quantization to express the Hamiltonian and wavefunctions, enabling a clear and concise representation of the electronic states. The Hamiltonian we consider includes all two-electron interactions in the Fock space that appear in the two-orbital model of the Heitler-London type.

One of the key aspects we explore is the concept of the bonding characteristics, namely covalency, atomicity, and ionicity, within the context of molecular dissociation. By examining the bonding factors as a function of interatomic distance, we provide an insight into the nature of chemical bonding and the evolution between different physical regimes. The analysis is based on the exact solutions of the extended Heitler-London model, allowing us to rigorously quantify the contributions of kinetic exchange interactions and effective Coulomb interactions to the overall bonding. Furthermore, we extend our investigation to the excited states of hydrogen molecules and discuss how they compare to the ground state.

I. METHOD

The total electronic energy of a system is expressed as the sum of the kinetic interaction part energy. The kinetic energy term in Hartree-Fock corresponds to the average kinetic energy of non-interacting electrons in the effective potential generated by the other electrons. On the other hand, the exchange kinetic energy refers to the contribution to the total kinetic energy that arises from the exchange interaction between identical particles, such as electrons. This is a quantum mechanical effect resulting from the indistinguishability of identical particles.

On the other hand, methods such as Configuration Interaction (CI), Coupled Cluster (CC), and Exact Diagonalization Ab Initio (EDABI)

To single out those exchange and other contributions we start from two general form of the Hamiltonian in the Fock space

$$\hat{\mathcal{H}} = \sum_{ij\sigma} t_{ij} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma} + \frac{1}{2} \sum_{\substack{ijkl \\ \sigma\sigma'}} V_{ijkl} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma'}^\dagger \hat{a}_{l\sigma'} \hat{a}_{k\sigma}, \quad (1)$$

where

$$t_{ij\sigma} \equiv \langle \phi_{i\sigma} | \mathcal{H}_1 | \phi_{j\sigma} \rangle, \quad (2)$$

and

$$V_{ijkl} = \langle \phi_{i\sigma} \phi_{j\sigma'} | V | \phi_{k\sigma'} \phi_{l\sigma} \rangle. \quad (3)$$

In these expressions, $t_{ij\sigma}$ represents the one-electron integrals, including kinetic energy and nuclear attraction, while V_{ijkl} are the two- electron integrals representing electron-electron repulsion. The operators $\hat{a}_{i\sigma}^\dagger$ and $\hat{a}_{j\sigma}$ are the creation and annihilation operators for electrons in orbitals i and j with spin σ .

The general N -particle state $|\Phi_N\rangle$ in Fock space can be related to the corresponding

N -particle wavefunction $\Psi_\alpha(\mathbf{r}_1, \dots, \mathbf{r}_N)$ in Hilbert space as follows [10]

$$|\Phi_N\rangle = \frac{1}{\sqrt{N!}} \int d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \Psi_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \hat{\Psi}_{\sigma_1}^\dagger(\mathbf{r}_1) \dots \hat{\Psi}_{\sigma_N}^\dagger(\mathbf{r}_N) |0\rangle. \quad (4)$$

where the field operator $\hat{\Psi}(\mathbf{r})$ is here approximated using a finite number M of wavefunctions $\{w_i(\mathbf{r})\}$

$$\hat{\Psi}(\mathbf{r}) \simeq \sum_{i=1}^M w_i(\mathbf{r}) \hat{a}_i, \quad (5)$$

where the Wannier-Mulliken function is taken in the following form of molecular orbitals

$$w_i(\mathbf{r}) = \beta(\psi_i(\mathbf{r}) - \gamma\psi_{i+1}(\mathbf{r})). \quad (6)$$

Such functions are normalized and orthogonal, which leads to the following expressions for β and γ

$$\beta = \frac{1}{\sqrt{2}} \sqrt{\frac{1 + \sqrt{1 - S^2}}{1 - S^2}} \quad (7)$$

$$\gamma = \frac{S}{1 + \sqrt{1 - S^2}}, \quad (8)$$

where $S = \langle \psi_1(\mathbf{r}) | \psi_2(\mathbf{r}) \rangle$ denotes the overlap integral.

The approximate N -particle wavefunction is then

$$\Psi_\alpha(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_{i_1, \dots, i_N=1}^M \langle 0 | \hat{a}_{i_N} \dots \hat{a}_{i_1} | \Phi_N \rangle w_{i_1}(\mathbf{r}_1) \dots w_{i_N}(\mathbf{r}_N). \quad (9)$$

In Fock space, the N -particle state is expressed as

$$|\Phi_N\rangle = \frac{1}{\sqrt{N!}} \sum_{j_1, \dots, j_N=1}^M C_{j_1 \dots j_N} \hat{a}_{j_1}^\dagger \dots \hat{a}_{j_N}^\dagger |0\rangle. \quad (10)$$

Substituting this into the N -particle wavefunction gives

$$\begin{aligned} \Psi_\alpha(\mathbf{r}_1, \dots, \mathbf{r}_N) = \\ \frac{1}{\sqrt{N!}} \sum_{i_1, \dots, i_N=1}^M C_{i_1 \dots i_N}(A, S) w_{i_1}(\mathbf{r}_1) \dots w_{i_N}(\mathbf{r}_N). \end{aligned} \quad (11)$$

where $C_{i_1 \dots i_N}(A, S)$ are the coefficients determined by the diagonalization. This represents the Configurational Interaction wavefunction for N particles distributed among M states, with A and S indicating antisymmetrization (Slater determinant) for fermions or symmetrization for bosons. In CI, the wavefunction is expressed as a linear combination of Slater determinants, and the coefficients $C_{i_1 \dots i_N}(A, S)$ are optimized variationally.

EDABI also involves diagonalizing the Hamiltonian matrix to find the exact wave function within a given basis set. The CI approach shares this feature but focuses on a finite basis set of M states, neglecting highly excited states to simplify the problem.

The CI method used here complements these approaches by determining the coefficients $C_{i_1 \dots i_N}$ through diagonalization in Fock space, potentially offering a more computationally efficient alternative while still capturing essential correlations in the system.

The full electronic Hamiltonian for the two-orbital model was derived and discussed earlier [7, 8, 11]. Here we present schematically all physical processes which are involved in this Hamiltonian in Fig. 1. In the figure ϵ_a denotes a single-particle energy of the electron in an atomic state and it is shown as an isolated electron with spin. The second microscopic parameter: hopping amplitude t represents electron hopping between two neighboring atoms. It is represented schematically in the Fig. 1 as an electron (green arrow) moving from one site to another. The U term accounts for the Coulomb repulsion between electrons on the same site. It is indicated in the Figure by a purple arrow representing the repulsion between two electrons at the same site (green arrows indicating opposing spins). The K term represents the Coulomb interaction between electrons on different sites. The figure illustrates this as a

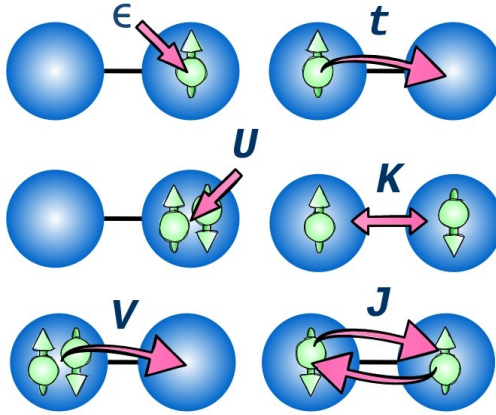


FIG. 1: Schematic illustration of various interaction processes within molecular systems, highlighting several key elements: single-particle excitation, electron hopping between adjacent sites, on-site Coulomb repulsion between electrons, direct exchange interaction between sites, inter-site Coulomb interaction, and indirect exchange interaction (superexchange). The green arrows represent particles with spin, while the pink arrows depict the pathways of these interactions.

repulsive force between electrons on adjacent sites (straight purple double arrow between two green arrows). The exchange integral J is shown in the figure a green arrows forming loops between two atoms occupied by two electrons with opposite spins suggesting the interaction involving an exchange of spin orientation. V is the so-called correlated hopping marked as a purple arrow from one atom to its neighbor indicating the hopping of an electron pair.

II. RESULTS

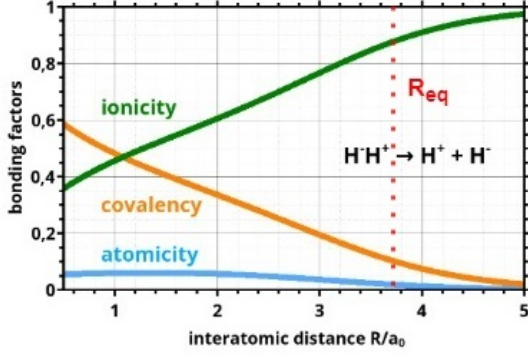
We discuss here results for hydrogen-based molecular systems like H_2^+ , H_2 , and H_2^- as functions of interatomic distance.

A. Hydrogen molecule excited states

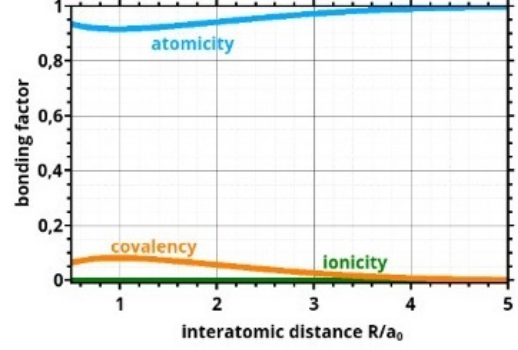
We begin by analyzing the spin-excited states of the hydrogen molecule. In this context, spin-excited states contain also states with total spin $S = 0$. Our previous works [] demonstrated that diagonalizing the Hamiltonian in second quantization form results in six states: two singlets, one triplet and triple degenerated singlet. This outcome is achievable even with a basis set consisting solely of $1s$ -type Slater orbitals.

In particular, we investigate these excited states utilizing our concepts of true covalency,

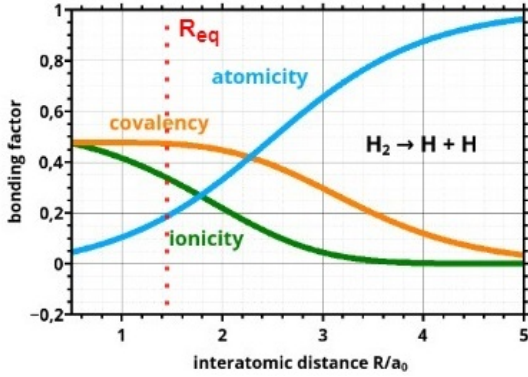
singlet $E_5 = 2\epsilon + (U+K)/2 + J + 2D$



singlet $E_6 = 2\epsilon + K - J$



singlet $E_G = 2\epsilon + (U+K)/2 + J - 2D$



triplet $E_2 = E_3 = E_4 = 2\epsilon + U - J$

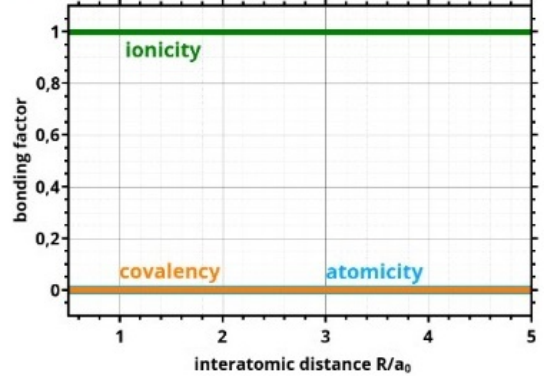


FIG. 2: The atomicity, ionicity, and covalency for various ground and spin-excited states of the hydrogen molecule (H_2) as functions of the interatomic distance R . The energy expressions for these states include contributions from kinetic energy, Coulomb interaction, and exchange terms.

atomicity, and ionicity (bonding factors) []. To this end, we present in Fig. 2 the bonding factors as functions of interatomic distance R for all six states of the hydrogen molecule, with energy formulas indicated on these plots. The bonding characteristics for those states are shown in Fig. 2.

The bottom-left panel shows the bonding characteristics for the ground state energy. As discussed earlier, the covalent contribution dominates at $R = R_{eq}$. However, there is a small admixture of atomic contribution. The ionic contribution is more noticeable than the atomic one, but as R increases, both covalent and ionic characters vanish, while the atomic character persists. The proper eigenvector in the second quantization can be written in the following form

$$\begin{aligned}
|6\rangle = & C \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle \\
& - I \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger + \hat{a}_{2\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger \right) |0\rangle,
\end{aligned} \tag{12}$$

where C and I as earlier denote covalent and ionic factors, respectively. The evolution from covalent-dominated bonding to the atomic limit is consistent with the intuitive picture resulting from the interpretation of the behavior of the binding energy curve, where in the limit $R \rightarrow \infty$ the molecule disperses into two individual atoms.

The top-left panel represents another one of the singlet states. In this case, ionicity contribution is dominant. The contribution of ionicity in this case is significantly smaller than for the ground state, which is obvious due to the nature of the wave function. As the interatomic distance increases covalency and atomicity as expected approach zero while ionicity reaches a value of one.

$$\begin{aligned}
|5\rangle = & C' \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle \\
& + I' \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger + \hat{a}_{2\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger \right) |0\rangle
\end{aligned} \tag{13}$$

in this case there are new functions C' and I' represent covalent and ionic factor, where $C' = 4(t + V)/\sqrt{2D(D - U + K)}$ and $I' = \sqrt{(D - U + K/2D)}$. As shown in Fig. 2, this state has a small minimum at $R = 3.5a_0$. The molecule excited to this state has a metastable state with an ionic character and in the limit of infinite R , separated atoms occurs, but unlike for the ground state, it results in H^+ and H^- ions rather than two neutral atoms.

The top-right panel also depicts the highest excited singlet state. In this state, atomicity is shown to be the dominant characteristic across the range of interatomic distances presented. Covalency and ionicity remain minimal, suggesting that the bonding in this excited state is predominantly characterized by atomicity. Three degenerated singlet eigenvectors are of the form

$$|1\rangle = \hat{a}_{1\uparrow}^\dagger \hat{a}_{2\uparrow}^\dagger |0\rangle, \quad (14)$$

$$|2\rangle = \hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger |0\rangle, \quad (15)$$

$$|3\rangle = \frac{1}{\sqrt{2}} \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \right) |0\rangle. \quad (16)$$

In this case, covalency, ionicity and atomicity depend only on mixing parameters.

State $|1\rangle$ represents a configuration where both electrons are in a spin-up state. This kind of configuration typically does not contribute to the covalent bond because it does not allow for the formation of resonating paired electrons due to the Pauli exclusion, which is a prerequisite for strong covalent bonding.

The triplet $|2\rangle$ is characterized by the fact that one electron is in the spin-up state and one is in the spin-down state. It partially allows for covalent bonding, but given that the spins are not paired in the same orbital, the bonding is not as strong as in the fully paired configuration.

The bottom-right panel represents a triplet state. This panel shows that the ionicity is equal to one while covalency and atomicity remain zero. The eigenvector for this state is as follows

$$|4\rangle = \frac{1}{\sqrt{2}} \left(\hat{a}_{1\uparrow}^\dagger \hat{a}_{1\downarrow}^\dagger - \hat{a}_{2\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger \right) |0\rangle \quad (17)$$

As in the previous case, bonding factors are only functions of mixing parameters.

One can see that in this wavefunction there is no covalent or atomic admixture. This state is also unstable, which leads to the conclusion that the molecule in this state is a kind of resonant structure between bound and free ionic forms.

Not only the wavefunction can be analyzed in the context of bonding characteristics, but energy can also be used for this purpose. Let us consider two similar cases of singlets: the ground state singlet and the excited singlet, the energy of which differs only by a factor of $2D$. In the first case, the energy contains a $+2D$ factor, and in the latter case, it is $-2D$.

The addition of $2D$ to the energy increases the contribution of the ionic interactions (related to U and K). As D is positive, adding it increases the separation of charges,

leading to a more ionic character where the molecule dissociates into ions H^+ and H^- .

Covalent State (bottom left): The subtraction of $2D$ from the energy term reduces the contribution of the ionic interactions, enhancing the resonant nature of the bond where the electrons are more shared between the atoms. This leads to a lower energy state typical of covalent bonds, from the molecule dissociates into neutral atoms ($H + H$).

In the case of the singlet on the top-right side of the panel in Fig. 2, the atomic character based on the energy is quite obvious. The energy equation includes the term K , which generally represents interatomic Coulomb interaction promoting atomicity, and $-J$, which is an exchange interaction term that tends to destabilize the singlet state and is not present in the wavefunction. The presence of K and $-J$ without any direct dependence on the intraatomic Coulomb interaction term U indicates that this state is more likely to retain atomic characteristics rather than to form strong covalent or ionic bonds. Stronger atomicity in the graph aligns with this, as the energy expression supports a state where atoms remain relatively independent.

B. Bonding as an energy competition

It is a well-known fact, as demonstrated by Ruedenberg in his seminal work [12], that covalent bonding in hydrogen molecules occurs as a result of the kinetic energy decreasing with a simultaneous increase in the negative direction in potential energy. However, there are papers stating that this mechanism is not true in general and there are some molecular systems with different mechanisms lying on the bottom of the covalent bonding []. Regardless of the successes achieved in explaining the mechanisms of chemical bonding, the problem of ambiguity in results persists, as in the case of the LiH molecule, where Molecular Orbital theory (MO) gives different results than Valence Bond theory (VB). This issue was the subject of research by M. Pendas et al. [2] and also part of our studies [7]. Furthermore, methods based on energy decomposition are not without flaws, as they heavily depend on the numerical methods they are based on, which was discussed in this work [13]. In this subsection, we propose an analysis of chemical bonding based on methods used in condensed matter physics, using the hydrogen molecule as an example.

To make this feasible, we start with the exact two-particle wave function, which was previously obtained by solving the Heitler-London-Slater model of the hydrogen molecule

[7]. Such wave function can be written as

$$\begin{aligned}
 \Psi_0(\mathbf{r}_1, \mathbf{r}_2) &= \frac{2(t+V)}{\sqrt{2D(D-U+K)}} \Psi_{cov}(\mathbf{r}_1, \mathbf{r}_2) \\
 &- \frac{1}{2} \sqrt{\frac{D-U+K}{2D}} \Psi_{ion}(\mathbf{r}_1, \mathbf{r}_2) \equiv \\
 &\equiv C\psi_{cov}(\mathbf{r}_1, \mathbf{r}_2) + I\psi_{ion}(\mathbf{r}_1, \mathbf{r}_2).
 \end{aligned} \tag{18}$$

In the given expression the wave function is expressed as a linear combination of two terms: $\psi_{cov}(\mathbf{r}_1, \mathbf{r}_2)$ and $\psi_{ion}(\mathbf{r}_1, \mathbf{r}_2)$. Covalent C and ionic I factors are functions of microscopic parameters introduced in the previous subsection.

We consider the physical picture of why the chemical homopolar bond is covalent when the kinetic exchange interaction is higher than the effective Coulomb interaction. To do that we examine coefficients of the wave function from Eq. (18), where all parameters were explained but the role of D can still be difficult to grasp. The expression $D = \sqrt{16(t+V)^2 + (U-K)}$ determines the energy denominator of the wave function. Because our goal is to study the bonding factor as the ratio of kinetic energy to potential energy one can write it in the form

$$\begin{aligned}
 D &= (U-K) \sqrt{1 + \left(\frac{4(t+V)}{U-K} \right)^2} \\
 &= (U-K) \sqrt{1 + \left(\frac{J_{kex}}{U-K} \right)^2} = \\
 &= E_{eff} \sqrt{1 + \left(\frac{J_{kex}}{E_{eff}} \right)^2},
 \end{aligned} \tag{19}$$

where D denominator is a function of kinetic exchange interaction J_{kex} and effective Coulomb interaction E_{eff} .

In the ionic regime, $(t+V)$ contribution should be smaller than $(U-K)$, whereas in the covalent regime, it is predominant. But, as one can expect, the ionic regime is unphysical as we consider the two-atomic homonuclear molecule. In the opposite case, $(t+V)$ contribution is of larger magnitude than $(U-K)$. Although, in general, the mechanism of covalent bond formation is consistent with that proposed by Reudenberg, there are fundamental differences between his and our solution. In Reudenberg's analysis, kinetic energy is the energy associated with the motion of electrons, whereas the exchange interaction en-

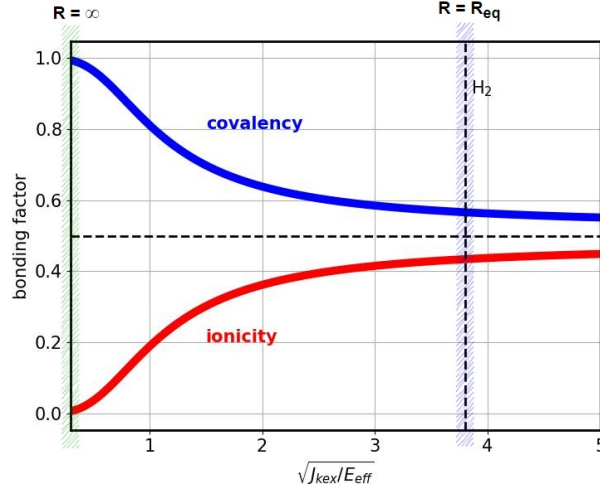


FIG. 3: Evolution of the bonding factors: covalency and ionicity for H_2 molecule with the square root of kinetic exchange and effective potential energy ratio. Two characteristic points are marked: the blue area is for that when $R = R_{eq}$, green area when $R \rightarrow \infty$.

ergy is related to the virtually resonating electrons in agreement with the understanding of covalent processes. The potential energy in Ruendenberg's analysis is calculated based on the electrostatic interactions between charged particles (nuclei and electrons) whereas in our case it is the difference between intraatomic and interatomic Coulomb repulsion, which is more natural to the discussion of ionic bonding.

In Fig. 3 evolution of the two bonding factors, covalency and ionicity, is shown with the square root of the kinetic exchange to potential energy ratio. In our case, covalency dominates for all values of the ratio, especially when it is maximal and equal to unity. This feature appears naturally as this point corresponds to the separated atoms limit, and this is classical covalency (a mix of true covalency and atomicity, as we shown in [8]). What is new in our approach is that instead of decomposing the total energy into kinetic and potential components, we introduce effective parameters J_{kex} and E_{eff} based on the exact solution of the extended Heitler-London model for the hydrogen molecule. It is also possible to carry out it for more complex molecules, but the analysis may be cumbersome to implement.

C. From one- to three-electron chemical bonding

Starting from the hydrogen molecular cation H_2^+ , with only one electron, we can write second quantized wave functions as follows

$$|\psi_+^{\text{H}_2^+}\rangle = \frac{1}{\sqrt{2}}(\hat{a}_1^\dagger + \hat{a}_2^\dagger) |0\rangle, \quad (20)$$

$$|\psi_-^{\text{H}_2^+}\rangle = \frac{1}{\sqrt{2}}(\hat{a}_1^\dagger - \hat{a}_2^\dagger) |0\rangle, \quad (21)$$

where only the bonding and antibonding orbitals appear. In this case, one can use relation from Eq. (9) to calculate the corresponding Wannier functions of the form

$$\psi_+^{\text{H}_2^+}(\mathbf{r}) = \frac{1}{\sqrt{2(1+S)}}(w_1(\mathbf{r}) + w_2(\mathbf{r})), \quad (22)$$

$$\psi_-^{\text{H}_2^+}(\mathbf{r}) = \frac{1}{\sqrt{2(1+S)}}(w_1(\mathbf{r}) - w_2(\mathbf{r})), \quad (23)$$

which are transformed into the bonding molecular wave function to the atomic-based form

$$\begin{aligned} \psi_-^{\text{H}_2^+}(\mathbf{r}) &= \frac{\beta}{\sqrt{2(1+S)}}((\phi_1(\mathbf{r}) - \phi_2(\mathbf{r})) \\ &+ \gamma(\phi_2(\mathbf{r}) - \phi_1(\mathbf{r})). \end{aligned} \quad (24)$$

In the case of the hydrogen molecule H_2 , the ground state wave function can be written similarly as in Eq. (18).

In the case of H_2^- ion, four states should be considered, leading to the construction of a 4×4 Hamiltonian, which yields two doubly degenerate states. For the lower energy state, the wave function in the language of second quantization takes the form

$$|\psi_G^{\text{H}_2^-}\rangle = \frac{1}{\sqrt{2}}(\hat{a}_{1\uparrow}^\dagger \hat{a}_{2\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger + \hat{a}_{1\downarrow}^\dagger \hat{a}_{2\uparrow}^\dagger \hat{a}_{2\downarrow}^\dagger) |0\rangle. \quad (25)$$

Equivalently this form has the following form in terms of the Wannier functions

$$\begin{aligned} \psi_G^{\text{H}_2^-}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \frac{1}{\sqrt{2}}(w_{1\uparrow}(\mathbf{r}_1)w_{2\uparrow}(\mathbf{r}_2)w_{2\downarrow}(\mathbf{r}_3) \\ &+ w_{1\downarrow}(\mathbf{r}_1)w_{1\uparrow}(\mathbf{r}_2)w_{1\uparrow}(\mathbf{r}_3)). \end{aligned} \quad (26)$$

It can be transformed to the three electron wave function consisting of linear combination of atomic functions

$$\begin{aligned}
\psi_G^{\text{H}_2^-}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = & \frac{\beta^3}{\sqrt{2}}(\phi_{1\uparrow}(\mathbf{r}_1)\phi_{2\uparrow}(\mathbf{r}_2)\phi_{2\downarrow}(\mathbf{r}_3) \\
& + \phi_{1\downarrow}(\mathbf{r}_1)\phi_{2\uparrow}(\mathbf{r}_2)\phi_{2\uparrow}(\mathbf{r}_3) \\
& + \phi_{1\uparrow}(\mathbf{r}_1)\phi_{1\downarrow}(\mathbf{r}_2)\phi_{2\uparrow}(\mathbf{r}_3) \\
& + \phi_{1\uparrow}(\mathbf{r}_1)\phi_{1\downarrow}(\mathbf{r}_2)\phi_{2\downarrow}(\mathbf{r}_3)).
\end{aligned} \tag{27}$$

We elaborate now on those three cases. The wave function for H_2^+ consists of partially covalent bonding where the single electron is spread over both nuclei, resulting in an intermediate bond strength. The bonding character is determined by both the overlap integral and mixing parameters (β, γ), whereas in the case of H_2 , it is a more complex function of microscopic (t, U, V, K), as well as the mixing parameters.

The wave function of H_2 represents a stronger covalent bond case with an admixture of the ionic part, absent in the single-electron of H_2^+ .

The three-electron wave function (Eq. (27)) reveals a more involved picture where distinguishing whether the chemical bond is covalent or ionic is not straightforward. It has a mixed resonant covalent-ionic bond character where two electrons always occupy one atom and the third is being transferred from one site to another. Such a process results in a more complex picture, in which the overall bond energy is reduced as shown in Tab. I.

Molecule	$R_{eq} (a_0)$	$E_{\text{bond}} \text{ (eV)}$	$\frac{J_{kex}}{E_{eff}}$
H_2^+	2.53	-1.7721	N/A
H_2	1.43	-4.0749	3.86
H_2^-	3.56	-2.1792	0.22

TABLE I: Comparison of bond lengths, E_{bond} , and $\frac{J}{E_{kex}}$ (on one particle) for H_2^+ , H_2 , and H_2^- .

The presented values of bond energy and its length indicate that in either H_2^+ and H_2^- ions are lower than in the case of H_2 whereas the value of the ratio of effective kinetic energy to potential energy significantly larger than 1. Interestingly, the ratio for H_2^- takes a value significantly lower than 1. We describe this reduction as the predominantly resonant character of the covalent-ionic bonding.

In the Fig. 4 the kinetic-exchange energy and the effective Coulomb interaction, both as

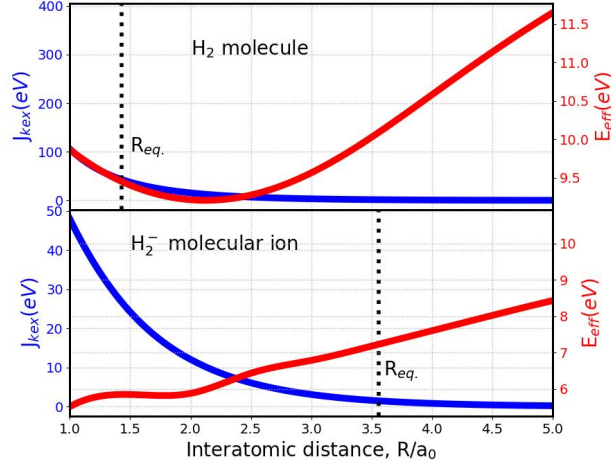


FIG. 4: Comparison of kinetic-exchange energy (left y-axis) and effective Coulomb interaction (right y-axis), both as a function of interatomic distance for H_2 molecule (top) and H_2^- (bottom). Red curve in the bottom figure is not smooth, likely caused by numerical artifacts introduced during the calculations.

a function of interatomic distance R , is compared for H_2 and H_2^- . From the bonding perspective, the plots provide an insight into the nature of bonding in those molecules. The H_2 molecule exhibits characteristics typical of covalent bonding, with the exchange interaction significantly higher than effective Coulomb interaction near the equilibrium distance (it is almost 4 times stronger). The effective kinetic energy decreases as the distance increases, still remaining larger than the effective potential energy. For the H_2^- the exchange interaction energy decreases steadily with the increasing R with the J_{kex}/E_{eff} ratio less than 1 around R_{eq} . One should note that this relation does not relate to the ionic bonding character.

TABLE II: Comparison of key parameters: orbital size, ground state energy per one particle, and microscopic parameters at the points of minimal energy for H_2 and H_2^- , respectively.

Parameter	H_2	H_2^-
E_G/N	-15.599	-12.87
α_0	0.839	1.25/1.33
t	-9.905	-1.487
U	22.490	13.99
K	13.007	6.705
V	-0.1578	-0.1265
J	0.2857	0.1238
$\frac{4(t-V)^2}{(U-K)}$	37.39	1.604

In Table II the basic quantities for H_2 and H_2^- are listed and compared at R_{eq} . For H_2 ,

the ground state energy per particle is lower by about 3 eV as compared to H_2^- . It means that the former is more stable.

A smaller orbital size in the case of H_2 suggests that the electrons on orbitals are more localized and closer to the nucleus. For the molecular ion, two α_0 values are given since the sizes of the 1s orbitals are not the same as they are occupied by either one or two electrons. The hopping parameters for these two systems indicate that electron mobility is significantly higher for H_2 (about four times higher). Additionally, Coulomb's repulsion magnitude is larger in the case of H_2 . Both interatomic and intraatomic repulsion values are approximately twice as high as the former. Similarly, the correlated hopping and exchange integrals are stronger in the neutral molecule.

Finally, the ratio $\frac{4(t-V)^2}{U-K}$ is 37.39 for H_2 and 1.604 for H_2^- , indicating a significantly stronger kinetic exchange interaction in the neutral molecule. This stronger interaction enhances effective electron sharing, promoting covalent bonding in H_2 .

III. CONCLUSIONS

We have analyzed here covalency, atomicity, and ionicity as the fundamental bonding characteristics for hydrogen-based systems: (H_2^+ , H_2 , and H_2^-). The results provide a nuanced view of how bonds evolved between the different regimes: covalent, atomic, and ionic as the atoms move closer or separate. In this work, we tested and developed the conceptual framework that employs the formalism of combined first- and second-quantization. We discussed the exact solution of the extended Heitler-London model for the three systems which allowed us to precise quantification of bonding contributions coming from the kinetic exchange and effective Coulomb interactions. The analysis concentrates on the chemical bonding resulting from competition between those two energies. By examining these interactions *vs.* R we offer an intuitive understanding of bonding nature, and in particular, highlight the evolution from covalent to ionic character.

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Oświadczenie o współautorstwie

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2. W szczególności, zaproponowane przeze mnie pojęcie atomowości, w analogii do wcześniejszych prac na temat lokalizacji Motta-Hubbarda w układach skondensowanych. Doktorant przeanalizował dokładnie numerycznie oraz analitycznie, co w konsekwencji doprowadziło do serii trzech prac oraz artykułu przeglądowego w Adv. Quant. Chem. Artykuł przeglądowy został napisany przez mnie przy pomocy ścisłej współpracy doktoranta na etapie technicznym. Zaproszenie do jego napisania otrzymał prof. E. Broclawik, która z kolei zaproponowała umieszczenie naszego dorobku w okresie wstępnym współpracy z Panią Prof. Broclawik nad wiązaniem wodorowym w naszym podejściu (projekt jeszcze niezakończony).
3. Wprowadzone nowatorskie pojęcie atomowości i naturalny sposób doprowadziło do ujęcia problemu wiązania chemicznego w języku opisów przez *macierz gęstości* i wprowadzenia pojęcia *entropii von Neumanna i korelacyjnego splątania*, co doktorant właśnie teraz skończył analizować szczegółowo (preprint). Dodatkowo doktorant zaproponował zmyślną transformację z języka orbitali molekularnych do atomowych, co pomogło w dalszej analizie.
4. Podkreślam, że wszystkie prace, pomimo tego że pierwszy draft prac i korespondencję wydawniczą prowadziłem osobiście, to współpraca z doktorantem była bardzo ścisła i poszczególne moje pomysły były gruntownie dyskutowane i szczegółowo opracowywane w bardzo ścisłej współpracy z doktorantem, ~~wraz~~ wliczając w pierwsze wersje prac wieloautorskich przedyskutowane (i poprawiane) z pozostałymi autorami. Numeryczna analiza została wykonana w całości przez doktoranta.



promotor rozprawy prof. dr hab. Józef Spalek

Oświadczenie o autorstwie prac

Oświadczam, że jestem współautorem następujących artykułów:

1. M. Hendzel, M. Fidrysiak, and J. Spalek, *Towards Complementary Characterization of the Chemical Bond*, J. Phys. Chem. Lett. **13**, 10261-10266 (2022),
2. M. Hendzel, M. Fidrysiak, and J. Spalek, *Many-particle covalency, ionicity, and atomicity on example of simple molecules*, J. Phys. B: At. Mol. Opt. Phys. **55**, 185101 (2022),

oraz rozdziału w książce

1. E. Broclawik, M. Fidrysiak, M. Hendzel, and J. Spalek, *Interparticle correlations and chemical bonding from physical side: Covalency vs atomicity and ionicity*, Adv. Quant. Chem. **87**, 351-373 (2023),

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Mój wkład w powstanie powyższej serii prac obejmuje udział w dyskusjach i korekcie manuskryptów.

Maciej Fidrysiak

Oświadczenie o współautorstwie

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Ewa Brocławik, Maciej Fidrysiak, Maciej Hendzel, Józef Spałek

Interparticle correlations and chemical bonding from physical side: Covalency vs atomicity and ionicity

Advances in Quantum Chemistry 87, 351-373 (2023)

Mój wkład w tę pracę polegał na istotnym udziale w dyskusjach nad naturą wiązania chemicznego, z których wyłonił się zamysł napisania tego interdyscyplinarnego artykułu. Jako chemik, wniosłam kilka pomysłów mających wpływ na kształt i zasięg pracy. Współuczestniczyłam w finalnych dyskusjach nad artykułem i właściwym sformułowaniem tez i wniosków oraz ostatecznym kształtem tekstu.



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