Degree of atomicity in the chemical bonding: Why to return to the H\textsubscript{2} molecule?

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We analyze two-particle binding factors for the case of H\textsubscript{2} molecule with the help of our original Exact Diagonalization Ab Initio (EDABI) 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 localization in many-particle systems. This additional characteristic introduces atomic ingredient into the essentially molecular states and thus eliminates a spurious behavior of the standard covalency factor with the increasing interatomic distance, as well as provides a physical reinterpretation of the chemical bond’s nature.

I. INTRODUCTION AND MOTIVATION

The concept of chemical bond as the fundamental quantum–mechanical characteristic of molecules such as H\textsubscript{2}, was firmly established by Heitler–London \textsuperscript{1} in 1927. This pioneering quantitative paper was based, by today’s standards, on the Hartree–Fock approximation for the two–particle wave function of the two electrons in H\textsubscript{2} molecule. Later, this function has been expressed by the corresponding atomic 1s hydrogen wave functions in the form of symmetrized product with 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 their superposition of those atomic wave functions into molecular single–particle wave functions centered on individual atoms, which have been subsequently put into a proper two–particle form \textsuperscript{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 later to it (Valence Bond Theory) \textsuperscript{2}. Theory of the bonding reached its mature form with an excellent series of papers by Kołos and Wolniewicz \textsuperscript{3, 4} who have included higher (virtually) excited states, supplemented with the nuclear vibrations \textsuperscript{5} to a fully quantitative form, which has been subsequently tested experimentally, since the bonding in H\textsubscript{2} molecule represents one of the tests of quantum–mechanical–theory verification in quantum chemistry \textsuperscript{6}.

In this brief paper we address, first of all, the question why we must realize that there is a need to return to the problem origins of the bonding nature in the H\textsubscript{2} 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 \textsuperscript{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 nonzero (actually, maximal) value of covalency in the limit of entirely separated atoms. Such an inconsistency has brought to our attention the old concept of Mott \textsuperscript{9}, concerning the electron localization in condensed matter physics (see also \textsuperscript{10, 11}). In effect, we have decided to introduce the concept of atomicity in the context of the correlated molecular electronic states \textsuperscript{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 the ionicity. Hence, in this paper we summarize and mainly interpret our recent results \textsuperscript{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 the next Section we briefly summarize our method and in Sec. III, regarded as the main part, we discuss our results and their meaning. This is followed by a brief Outlook. In general, the aim of the paper is to supplement previous papers \textsuperscript{7, 8} with 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 the hydrocarbons. The connecting link between the condensed matter localization and molecular atomicity may be then applied also to other nano–systems \textsuperscript{12, 13}.

II. METHOD

Our approach is based on Exact Diagonalization Ab Initio (EDABI) method which has been proposed and developed in our group \textsuperscript{12, 13}. Here we use this method to provide complementary bonding characteristics on example of H\textsubscript{2} molecule. The starting Hamiltonian, containing

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where $H.c.$ denotes the Hermitian conjugation, $\hat{a}_{i\sigma}^\dagger$ a fermionic annihilation (creation) operators for state $i$ and spin $\sigma$, and $\hat{n}_{i\sigma} \equiv \hat{a}_{i\sigma}^\dagger \hat{a}_{i\sigma}$. 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 $\sigma_i$ 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 (Eq. (1)) one can write ground state wave function of the ground–state two–particle wave function, obtained in the form

$$\psi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) + \psi_{\text{ion}}(\mathbf{r}_1, \mathbf{r}_2),$$

where ionic and covalent parts are

$$\psi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{2(t + V)}{\sqrt{2D(D - U + K)}} [w_1(\mathbf{r}_1)w_2(\mathbf{r}_2)],$$

$$\psi_{\text{ion}}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{2} \sqrt{\frac{D - U + K}{2D}} [w_1(\mathbf{r}_1)w_2(\mathbf{r}_2)]$$

with

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

and

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

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 $\beta$ and $\gamma$ as mixing parameters. These atomic functions can be in the form of Slater or Gaussian form (Slater or Gaussian orbitals, STO or GTO). Furthermore, Eqs. (2) and (3) can be rewritten, with use of Eq. (5), in the following way:

$$\psi_{\text{cov}}(\mathbf{r}_1, \mathbf{r}_2) = (C\beta^2(1 + \gamma^2) - 2\gamma I\beta^2) [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)]$$

$$+ \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2))][\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2)],$$

and

$$\psi_{\text{ion}}(\mathbf{r}_1, \mathbf{r}_2) = (I\beta^2(1 - \gamma^2) - 2\gamma C\beta^2) [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)]$$

$$+ \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2))][\chi_\downarrow(1)\chi_\uparrow(2) - \chi_\uparrow(1)\chi_\downarrow(2)],$$

where $C$ and $I$ are coefficients from (2) and (3), respectively.

Parenthetically, for the sake of comparison one can write postulated VB two–particle wave function

$$\psi_{\text{cov}}^{VB}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2(1 + S^2)}} [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)]$$

$$\times \frac{1}{\sqrt{2}} [\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2)],$$

and

$$\psi_{\text{ion}}^{VB}(\mathbf{r}_1, \mathbf{r}_2) = [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)] + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2))$$

$$\times \frac{1}{\sqrt{2}} [\chi_\downarrow(1)\chi_\uparrow(2) - \chi_\uparrow(1)\chi_\downarrow(2)],$$

where $S$ is the overlap between the neighboring atomic wave functions. However, the total wave function, consisting of sum of the (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 the ionicity and covalency [8] and define atomicity [7], the last is the complementary characteristic to the two former.

A remark is in place at this point. As said above, he two–electron component wave functions (8) and (9) have formally the same form as their VB counterparts (8) and (9), albeit with the two principal differences. First, the coefficients before the covalent and ionic parts, $\psi_{\text{cov}}$ and $\psi_{\text{ion}}$, are different as they contain all Coulomb–interaction terms between the particles composing the bond. Second, the orbital size ($\alpha^{-1}$) of the original atomic wave functions, composing those functions are 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.
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 main text.

In the next Section we discuss our results, after minimizing the ground state energy, \( E_{G}[\psi_G(\alpha)] = \langle \psi_G(\alpha) | H | \psi_G(\alpha) \rangle / \langle \psi_G(\alpha) | \psi_G(\alpha) \rangle \), with respect to \( \alpha \) and evaluating explicitly the microscopic parameters for the optimal value of \( \alpha = \alpha_0 \).

III. RESULTS AND DISCUSSION

We now proceed with the presentation of our results, followed up by their discussion. In Fig. 1 we illustrate the interatomic distance, \( R \), 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 \( \frac{2|t + V|/(U - K)}{R} \) 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) describes then 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 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 this Figure also 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 \( R \to \infty \) (\( R > R_{\text{Mott}} \)).

To restore physical meaning to the covalency we make use of our earlier observation that in \( R \to \infty \) 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 ionicity \( \gamma_{\text{ion}} \) from the covalency presented in Fig. 3 by extracting from the corresponding expression (6) the part taken for \( \gamma = 0 \) at given \( R \) (not only in the atomic limit). As a result, we get the true covalency versus atomicity, both as function of \( R \), depicted in Fig. 3. The ionicity remains without change, since it expresses the complementary factor of bonding — the double occupancy. One should stress the fundamental difference between the covalency and ionicity factors, \( \gamma_{\text{cov}} \) and \( \gamma_{\text{ion}} \), 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 \( \gamma_{\text{cov}} + \gamma_{\text{ion}} + \gamma_{\text{sat}} = 1 \) (for details see [7]). It is remarkable, that the Mott–Hubbard criterion for localization meets the point where the defined atomicity \( \gamma_{\text{sat}} \) and redefined covalency \( \gamma_{\text{cov}} \) are equal. Obviously, for larger \( R \) values, the atomicity prevails, whereas the...
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 shown in Fig. 1.

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 Koles–Wolniewicz (K–W) result.

| Method          | 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                     |

ionicity $\gamma_{\text{ion}}$ (not shown) decreases steadily to zero.

To illustrate our results by the 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 $\gamma$ is admixture of 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 of 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 prospective, 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 H$_2$ molecule (cf. Table I), as well as have singled out the bond characteristics (Table II). Additionally, we have supplemented these results with the true covalency, atomicity, and ionicity factors in Tables III/IV.

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.

| Method          | 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 $R = R_{\text{Bond}}$ 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 Theory (with and without renormalizing orbital size).

|                          | Covalency | Ionicity |
|--------------------------|-----------|----------|
| Full Hubbard Model       | 0.59      | 0.41     |
| Hubbard Model            | 0.86      | 0.14     |
| Valence Bond Theory      | 0.52      | 0.48     |
| Valence Bond Theory (renormalized) | 0.63 | 0.37 |
| Space Bonding Descriptor | 0.57      | 0.43     |
FIG. 5. Probability density profiles according to Valence Bond (VB) approach — upper panel, as well as those with taking the two–particle wave functions (2) and (3). The interatomic distance $R$ is specified.

TABLE IV. True binding characteristics for $\text{H}_2$ 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     |

IV. OUTLOOK

The principal concept introduced in our approach [8] is the concept of atomicity in nominally covalent bond of $\text{H}_2$ (albeit, also with a nontrivial degree of ionicity). One should be aware of the fact that hydrogen molecule, in the hypothetical so far limit $R \to \infty$, 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 finite distance when the particles interact, what 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 finite distance should be regarded as intuitive in nature, even though it helps to remove the principal inconsistency in evolution of the covalency as a function of interatomic distance.

Finally, the overall behavior of the $\text{H}_2$ system is illustrated in Fig. 5, where the probability density profiles are shown for the three interatomic distances specified: At equilibrium bond distance ($R = 1.43 a_0$), at the Mott–Hubbard boundary ($R = 2.3 a_0$), and in the asymptotic regime of large distances ($R = 4 a_0$). The density profiles are artificially distorted from their almost spherical shapes by the choice of scale to expose the details of the density isolines in that case. One sees 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.
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