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Degree of Atomicity in the Chemical Bonding: Why Return to the H_2 Molecule?

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We analyze two-particle binding factors for the case of the H_2 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 H_2 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 H_2 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 H_2 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 H_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 [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 H_2 molecule. The starting Hamiltonian, containing all Coulomb interactions, formulated in the second quantization language, is of the form

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

where h.c. denotes the Hermitian conjugation; $\hat{a}_{i\sigma}$ ($\hat{a}^\dagger_{i\sigma}$) are fermionic annihilation (creation) operators for state i and spin σ; $\hat{n}_{i\sigma} \equiv \hat{a}^\dagger_{i\sigma}\hat{a}_{i\sigma}$ 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 $\hat{\boldsymbol{S}}_i \equiv \frac{1}{2}\sum_{\alpha\beta} \hat{a}^\dagger_{i\alpha} \boldsymbol{\sigma}_i^{\alpha\beta} \hat{a}_{i\beta}$ 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 $\propto J^H_{ij}$, 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 $\psi_G(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{\text{cov}}(\boldsymbol{r}_1, \boldsymbol{r}_2) + \psi_{\text{ion}}(\boldsymbol{r}_1, \boldsymbol{r}_2)$, where ionic and covalent parts are

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

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

with

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

and

$$w_{i\sigma}(\boldsymbol{r}) = \beta\Big(\phi_{i\sigma}(\boldsymbol{r}) - \gamma \phi_{j\sigma}(\boldsymbol{r}) \Big), \tag{5}$$

with $i = 1$, $j = 2$ or $i = 2$, or $j = 1$, in this case. The two functions are molecular functions and come out naturally within our method, in which the two neighboring atomic functions $\phi_i(\boldsymbol{r})$ 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]

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

and

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

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

$$\begin{aligned}\psi^{\text{VB}}_{\text{cov}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = {}& \frac{\Big[\phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) + \phi_2(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2) \Big]}{\sqrt{2(1+S^2)}} \\ & \times \frac{1}{\sqrt{2}} [\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2)],\end{aligned} \tag{8}$$

and

$$\begin{aligned}\psi^{\text{VB}}_{\text{ion}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = {}& \Big[\phi_1(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2) + \phi_2(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) \Big] \\ & \times \frac{1}{\sqrt{2}} \Big[\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\downarrow(1)\chi_\uparrow(2) \Big],\end{aligned} \tag{9}$$

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, $\psi_{\rm cov}$ and $\psi_{\rm ion}$, 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

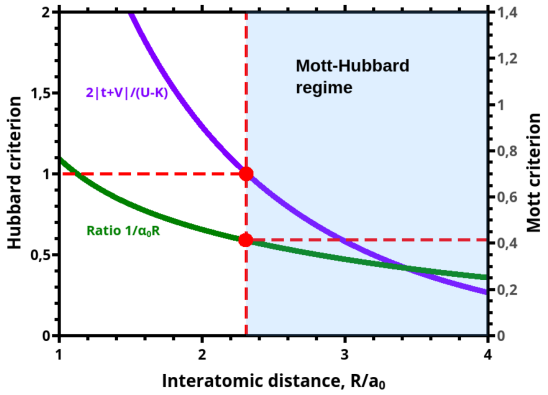

Fig. 1. Mott (green, lower) and Hubbard (purple, upper) lines with the marked corresponding Mott and Hubbard criteria of localization. The shaded area to the right of $R = R_{\rm Mott}$ represents the region with steadily increasing atomicity with increasing R. For details see the main text.

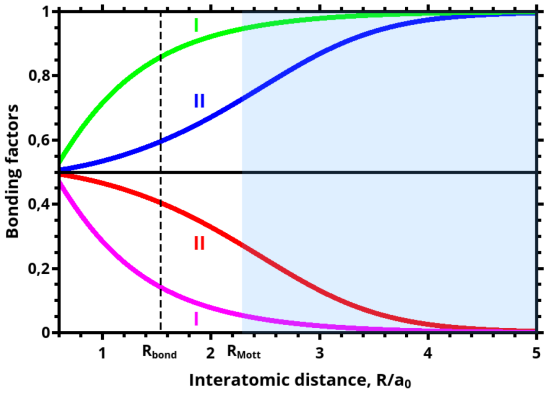

Fig. 2. Comparison of starting binding factors (ionicity and standard covalency) vs interatomic distance. Those microscopic parameters are determined, respectively: from Hubbard model — curves I, extended Hubbard model — curves II. The shaded area corresponds to the Mott–Hubbard ("Mottness") regime,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

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 $R \to \infty$ ($R > R_{\rm Mott}$).

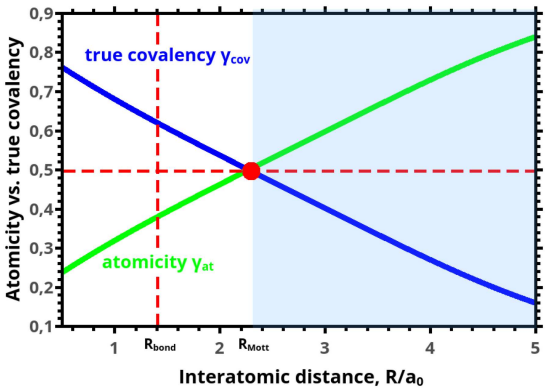

Fig. 3. Participation of true covalency and atomicity in the resultant correlated state of electrons in H_2. Note that the two curves cross the marked point, which corresponds accurately to the one shown in Fig. 1.

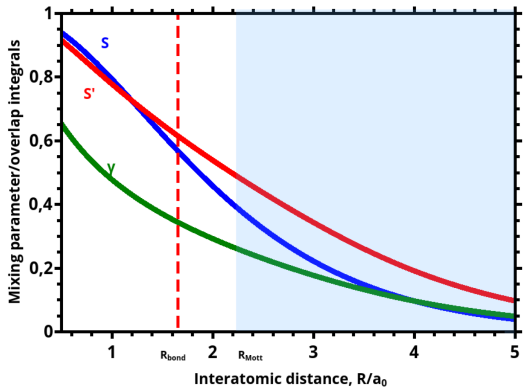

Fig. 4. Single-particle mixing parameter γ, overlap integral without orbital size renormalization S, and orbital size calculated for renormalized orbital size S' versus interatomic distance R. They evolve continuously as a function of interatomic distance. The dashed vertical line marks, as in all previous 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 $R \to \infty$ 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 *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 $E_{\mathrm{HF}} - E$, 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 $R = R_{\mathrm{Bond}}$ 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

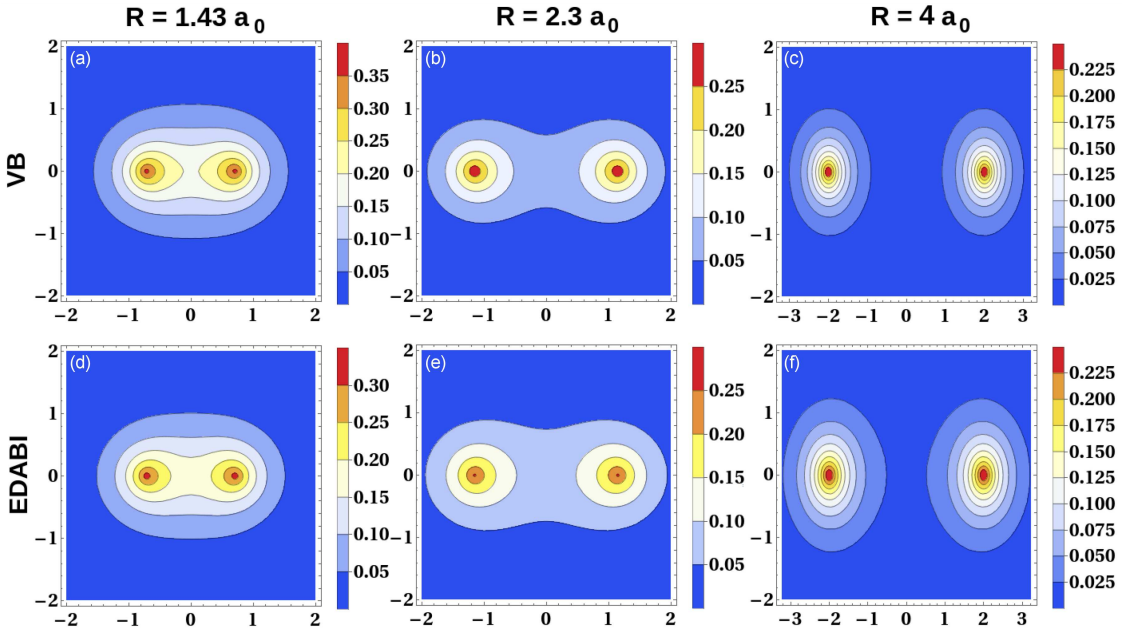

Fig. 5. Probability density profiles according to valence bond (VB) approach panels (a)–(c)), as well as those taking the two-particle wave functions (2) and (3) (panels (d)–(f)). The interatomic distance R is specified.

the covalency and ionicity factors, $\gamma_{\rm cov}$ and $\gamma_{\rm ion}$, shown in Fig. 2 and those exhibited in Fig. 3. In the former case, we have that $\gamma_{\rm cov} + \gamma_{\rm ion} = 1$, whereas in the present situation, $\gamma_{\rm cov} + \gamma_{\rm ion} + \gamma_{\rm at} = 1$ (for details, see [7]). It is remarkable that the Mott–Hubbard criterion for localization meets the point, where the atomicity $\gamma_{\rm at}$ and redefined covalency $\gamma_{\rm cov}$ are equal. Obviously, for larger R values, the atomicity prevails, whereas the ionicity $\gamma_{\rm ion}$ (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 $R = R_{\rm Bond}$ and $R = R_{\rm Mott}$. 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 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 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 $R > R_{\mathrm{Mott}}$ 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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