



Chemical bonding without orbitals

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ABSTRACT

This work presents an implementation of the original orbital-free Hohenberg-Kohn density functional theory in a form that is able to predict chemical bonding in molecules. The method is completely parameter-free and does not require analytical functional approximations. Instead, the proposed method is based on the idea that atoms are meaningful pieces of a molecule and thus, a promolecule, build from frozen spherical atomic entities, serves as a suitable model for the latter. This idea is imposed on the physical equations, originating from density functional theory converted into a bifunctional formalism.

The viewpoint proposed in this study offers a new strategic way of subsequent approximation levels in orbital-free density functional theory. In this work the zeroth order approximation is shown to predict chemical bonding in molecules, providing a concept of the chemical bond without involving orbitals.

1. Introduction

The chemical bond [1–4] is a fundamental concept in chemistry and related sciences. Taking a very simplistic standpoint, the chemical bond somehow serves as glue, binding together the partaking atoms [5,6]. One part of chemistry is to define and quantify chemical bonding in order to predict molecular stability and how the system will undergo possible changes induced by the environment. Unfortunately, the definition of that chemical bonding is ambiguous. This is due to the fact that atoms in molecules are no physical entities. From a puristic standpoint, the molecule is defined once the number of electrons and the nuclear positions are given. By solving the quantum mechanical equations [7,5], the statistical distribution of the electrons in the field of the nuclei is determined. In that spirit, the molecule only consists as a whole, namely of all nuclei and all electrons, whereby the latter are usually (but not necessarily) described in terms of orbitals. The equations describe all orbitals at once and their solutions extend over the whole space. This form of wavefunction based quantum mechanics is said to be non-local [7], meaning that changes induced at one position in space might cause noticeable effects far away from the initial position. Such a non-local form of quantum mechanics is not suited for an atomic fragment approach, where those fragments are thought as being subjected to a physical interaction.

Indeed a local form of quantum theory is needed, further allowing for a meaningful separation into atomic fragments. This local form of quantum theory is called density-functional theory (DFT) [8,9]. In the Hohenberg-Kohn variant [10], the system is described by the electron density itself, rather than by orbitals. This theory is guided by a local

causality principle [11–18] (effective interactions decrease with increasing distance) and, as will be shown in this work, allows for a meaningful separation into atomic fragments, while keeping the initial physical equations unaltered. Although the original ideas of Hohenberg and Kohn dates back more than fifty years, a widespread use of orbital-free DFT has been hampered by the lack of sufficiently accurate functional approximations for the kinetic energy [19]. Whereas considerable progress has been made for one-dimensional systems [20], the treatment of molecular systems or solids requires appropriate three-dimensional functional approximations. First work was based on conventional gradient expansions [21–32], whereas recent functional development is mainly focused on techniques based on the generalized-gradient-approximation motivated by conjoint arguments [33,34] or the fulfillment of additional constraints [35,36,19]. Information-theory motivated functionals [37–39], functionals based on response theory [40,41], and expansions in terms of moment densities [42] have been studied. Recently, a very promising approach based on the Liu-Parr power series expansion [43] has been suggested by Ludeña and coworkers [44,45], including a detailed investigation concerning the ability of their ansatz to represent the atomic shell structure. Despite much efforts, it still remains difficult to design appropriate functional approximations, which yield properly structured electron densities from variational procedure [46]. This failure can be attributed to an insufficient incorporation of the Pauli exclusion principle [27,8,19] in the Pauli kinetic energy and the corresponding Pauli potential [47]. Both terms were intensively studied in the literature [48–56] as they represent the unknown part of the kinetic energy functional and the corresponding potential, respectively. As a consequence, there is up to

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now no reliably working orbital-free density functional implementation for the waste variety of chemical substances. There are a few noticeable exceptions treating variational orbital-free density functional approximations [57–61]. However, widespread applications covering all types of chemical substances without need of recursive adjustment of technical details are still out of reach.

This work offers a new strategy in orbital-free density functional theory based on the reformulation in terms of bifunctionals.

2. Formulation of the problem

In 1964 Hohenberg and Kohn (HK) rigorously founded density functional theory (DFT) [10]. In their seminal paper they proved the one-to-one correspondence between the energy E of the system and the external potential due to the nuclei v_Z (first HK theorem) as well as the minimum principle of that energy functional $E[\rho]$ (second HK theorem) for all electron densities ρ that are associated with some external potential. According to the first HK theorem, the electronic energy of a system $E[\rho]$, given as the sum of the kinetic energy $T[\rho]$, the Coulomb repulsion between the electrons $V_{ee}[\rho]$, and the electron-nuclear attraction energy $V_Z[\rho]$, can be expressed as a density functional:

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_Z[\rho] \quad (1)$$

The second HK theorem tells how to reach that electron density, for which this energy expression is minimal. For the minimizing electron density, the functional derivative is zero, since infinitesimal changes of ρ do not alter the energy value at the minimum:

$$0 = \frac{\delta(E[\rho] - \mu(N - \int \rho(\vec{r}) d\vec{r}))}{\delta\rho} \quad (2)$$

In the above equation the chemical potential μ has been introduced as Lagrange multiplier for an additional constraint, namely the search is performed for that electron density, which integrates to the number of electrons N in the system. Inserting the energy from Eq. (1) yields:

$$0 = \frac{\delta T[\rho]}{\delta\rho} + \frac{\delta V_{ee}[\rho]}{\delta\rho} + \frac{\delta V_Z[\rho]}{\delta\rho} - \frac{\delta\mu(N - \int \rho(\vec{r}) d\vec{r})}{\delta\rho} \quad (3)$$

$$0 = v_T + v_{ee} + v_Z - \mu.$$

The last line is known as Euler equation [8]. It contains the functional derivatives, the potentials, of the respective energy expressions. Hereby v_T is the functional derivative of the kinetic energy, v_{ee} the potential of the electronic repulsion, and v_Z is the nuclear potential.

The electron nuclear attraction energy is known exactly as electron density functional:

$$V_Z[\rho] = \int \rho(\vec{r}) v_Z(\vec{r}) d\vec{r} \quad (4)$$

with the nuclear potential of a molecule is given by the superposition $v_Z(\vec{r}) = \sum_A v_Z^A(\vec{r})$ of all atomic nuclear potentials $v_Z^A(\vec{r}) = -Z_A/|\vec{r} - \vec{R}_A|$, with Z_A being the nuclear charge and \vec{R}_A the nuclear coordinates.

If all energy terms were known analytically as density functional expressions, a quantum mechanical DFT calculation would only require searching for that electron density distribution for which the Euler equation, cf. Eq. (3), equals zero everywhere in space. The potentials in Eq. (3) depend on the electron density. The equation is fulfilled only for the minimizing electron density. Unfortunately, no widely applicable kinetic energy functional able to predict chemical bonding in molecules has been found yet. For that reason, in the current form of Kohn-Sham (KS) DFT, only the electron repulsion V_{ee} is approximated and the kinetic energy T is still given in terms of KS orbitals.

3. Reformulation in terms of bifunctionals

The conventional strategy in the design of energy functionals is to

start with an ansatz for the energy in the form of an analytical expression that is an integral over a function f , which in some way contains the electron density (and possibly some other ingredients):

$$F[\rho] = \int f(\rho(\vec{r}), \dots) d\vec{r} \quad (5)$$

From that functional, the potential, being the functional derivative, is obtained analytically, cf. Eq. (3). As mentioned, no ansatz for the kinetic energy has been found that is able to predict chemical bonding in molecules. This failure is mainly due to the aspect that the derived kinetic potentials [62] yield electron densities missing proper atomic shell structure [63–65].

In the following the original problem of density functional theory will be (exactly) reformulated in terms of bifunctionals. The chosen bifunctional construction allows to approximate potentials (rather than energy expressions) and subsequently evaluate the energy.

A bifunctional expression exploiting the homogenous scaling behavior of a functional

$$F[\rho_\lambda] = \lambda^k F[\rho] \quad (6)$$

with $\rho_\lambda = \lambda^2 \rho$ is of the following form [66]:

$$F\left[\rho, v\right] = -\frac{1}{k} \int \rho(\vec{r}) \vec{r} \cdot \vec{\nabla} v(\vec{r}) d\vec{r} \quad (7)$$

The homogenous scaling behavior is known [66] for the non-interacting kinetic energy T_s [67], hereby $k = 2$, and thus:

$$T_s\left[\rho, v_s\right] = -\frac{1}{2} \int \rho(\vec{r}) \vec{r} \cdot \vec{\nabla} v_s(\vec{r}) d\vec{r} \quad (8)$$

the non-interacting kinetic energy can be expressed via its functional derivative v_s , also called Kohn-Sham potential. The non-interacting kinetic energy T_s is the largest part of the kinetic energy $T = T_s + T_c$. The missing term, the correlation part of the kinetic energy T_c has been shown to be nearly negligible [68–70]. In addition, the scaling behavior of the classical Coulomb repulsion between electrons, called Hartree energy V_H , and of the exchange energy V_X is known [66] to be $k = 1$. Thus, there sum, noted V_{HX} , is given by:

$$V_{HX}\left[\rho, v_{HX}\right] = - \int \rho(\vec{r}) \vec{r} \cdot \vec{\nabla} v_{HX}(\vec{r}) d\vec{r} \quad (9)$$

with v_{HX} being the functional derivative of V_{HX} with respect to ρ . The energy V_{HX} represents the largest part of the quantum mechanical electron-electron repulsion, $V_{ee} = V_{HX} + V_c$. The Coulombic part of the correlation energy V_c does not exhibit homogeneous scaling behavior [66], and thus, cannot be expressed in the chosen bifunctional formalism. The sum of both correlation effects $E_c = T_c + V_c$ is named correlation energy [8].

Finally, the electronic energy of a molecule can be exactly expressed in terms of the bifunctionals:

$$E[\rho] = T_s[\rho, v_s] + V_{HX}[\rho, v_{HX}] + V_Z[\rho, v_Z] + E_c[\rho] \quad (10)$$

and the electron correlation $E_c[\rho]$, given in form of a conventional density functional. The above expression is an exact reformulation of the original DFT problem, allowing to approximate functional derivatives instead of the functionals themselves. Notice that, in order for the bifunctional expression to be correct, the potential and the electron density must be related via the corresponding Euler equation.

4. The chemical bond in the atomic fragment approximation

From a chemist's viewpoint it seems natural to interpret [71–73] large aggregates as being composed from atomic fragments [74–77] that somehow hold together. In the following it is shown how to link such a viewpoint with the quantum mechanical equations based on the

bifunctional formalism and the atomic fragment approach.

A so-called promolecule [78,76] is the sum of (usually spherical) atoms centered at the positions of the nuclei for the actual molecule of interest. Consequently, properties of the promolecule are evaluated as a sum over atomic contributions. Thus, the promolecular density is given:

$$\rho^{\text{prom}}(\vec{r}) = \sum_A \rho^A(\vec{r}) \quad (11)$$

as sum of atomic densities $\rho^A(\vec{r})$. Equally, the promolecular potentials $v_s^{\text{prom}}(\vec{r})$ and $v_{\text{HX}}^{\text{prom}}(\vec{r})$ can be determined from the individual atomic contributions:

$$v_s^{\text{prom}}(\vec{r}) = \sum_A v_s^A(\vec{r}), \quad (12)$$

$$v_{\text{HX}}^{\text{prom}}(\vec{r}) = \sum_A v_{\text{HX}}^A(\vec{r}). \quad (13)$$

In the zeroth order fragment approximation, the electronic correlation is neglected and the promolecule serves as model for the true molecular system. All physical properties are evaluated from the promolecular density-potential pair via the bifunctional formalism. Thus, the electronic energy of a molecule in the zeroth-order fragment approach is given by:

$$E[\rho^{\text{prom}}] = -\frac{1}{2} \int \rho^{\text{prom}}(\vec{r}) \vec{r} \cdot \vec{\nabla} v_s^{\text{prom}}(\vec{r}) d\vec{r} - \int \rho^{\text{prom}}(\vec{r}) \vec{r} \cdot \vec{\nabla} v_{\text{HX}}^{\text{prom}}(\vec{r}) d\vec{r} + \int \rho^{\text{prom}}(\vec{r}) v_Z(\vec{r}) d\vec{r}. \quad (14)$$

In the above equation, the first term represents the kinetic energy of the electrons, the second term the electronic repulsion, and the third term the attraction between the electrons and the nuclei.

Within the proposed bifunctional approach, the promolecule carries the mandatory prerequisites to describe chemical bonding, namely the dependence of the energy on the nuclear coordinates. This is schematically shown in Fig. 1 for the electron-nuclear attraction energy V_Z evaluated from a promolecule AB. Consider the case that the atom A is alone in space. The atomic density ρ^A depicted by the solid black line exhibits a maximum at the position of the nucleus A and decays exponentially in space. The nuclear potential v_Z^A , shown by the dashed black line, is equally centered at the position of the nucleus A.

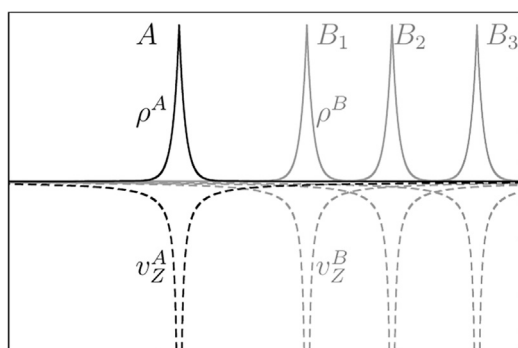


Fig. 1. Schematic representation of an atom versus promolecule and the resultant electron-nuclear attraction energy V_Z . Considering only the black lines, the atom A is alone in space. In that case the electron density ρ^A (shown by the solid line) is multiplied with the nuclear potential v_Z^A , yielding the nuclear attraction energy, $V_Z^A = \int \rho^A v_Z^A d\vec{r}$, of atom A. In case that a second atom B is located in proximity (shown in grey for three different positions), the nuclear attraction energy is summed from the individual atomic contributions ($V_Z^A + V_Z^B$), but also from the interaction term $V_Z^{\text{int}} = \int (\rho^A v_Z^B + \rho^B v_Z^A) d\vec{r}$, that stem from the atomic density ρ^A in the presence of the nuclear potential v_Z^B located at atom B, and vice versa. Although, both, atomic densities and potentials, are not allowed to adapt (in the promolecule they remain atomic-like), the interaction energy V_Z^{int} depends on the internuclear distance R_{AB} . This is mandatory for the description of chemical bonding.

Evaluation of the electron-nuclear attraction energy requires multiplication of the electron density with the potential and integration over the whole space, $V_Z^A = \int \rho^A v_Z^A d\vec{r}$.

In case, that the promolecule is considered, a second atom, here B, is placed in proximity to the atomic nucleus A. The respective density and potential are depicted in grey. Fig. 1 exemplarily contains three different positions for the location of B. Notice, that the atomic densities (and the corresponding potentials) remain atomic-like. However, the electron-nuclear attraction energy evaluated for the promolecule covers, besides the individual atomic contributions ($V_Z^A + V_Z^B$), the interaction term $V_Z^{\text{int}} = \int (\rho^A v_Z^B + \rho^B v_Z^A) d\vec{r}$, originating from the presence of the neighboring nuclear potentials in the decaying region of the respective atomic densities. Those terms depend on the internuclear distance and is mandatory to recover chemical bonding from a given ansatz.

In the following, it is shown that the proposed fragment model, is able to predict bonding for a dimer AB. The binding energy $E^{\text{int}}(R_{AB}) = E^{\text{dim}} - \sum E^A$ is defined as the difference between the energy of the dimer E^{dim} and the sum of isolated (non-interacting) atomic energies E^A . Hereby, the total energy of the dimer consists of the electronic energy $E[\rho^{\text{prom}}]$, cf. Eq. (14), and the repulsion between the two nuclei $Z_A Z_B / R_{AB}$. Thus, the binding energy is given by:

$$E^{\text{int}}(R_{AB}) = E[\rho^{\text{prom}}] + \frac{Z_A Z_B}{R_{AB}} - (E[\rho^A] + E[\rho^B]) \quad (15)$$

Exploiting the fact that atomic fragments in a promolecule still fulfill the individual atomic Euler equations, finally results in the binding energy of a promolecule AB as given by the zeroth order fragment approach:

$$E^{\text{int}}(R_{AB}) = -T^{\text{int}} + V_{ZZ}^{\text{int}} + \frac{Z_A Z_B}{R_{AB}} \quad (16)$$

with:

$$T^{\text{int}} = -\frac{1}{2} \int \rho^A \vec{r} \cdot \vec{\nabla} v_s^B(\vec{r}) d\vec{r} - \frac{1}{2} \int \rho^B \vec{r} \cdot \vec{\nabla} v_s^A(\vec{r}) d\vec{r} \quad (17)$$

and

$$V_{ZZ}^{\text{int}} = \int \rho^A [\vec{r} \cdot \vec{\nabla} v_Z^B(\vec{r}) + v_Z^B(\vec{r})] d\vec{r} + \int \rho^B [\vec{r} \cdot \vec{\nabla} v_Z^A(\vec{r}) + v_Z^A(\vec{r})] d\vec{r} \quad (18)$$

Notice, that the binding energy based on the promolecule can thus solely be expressed with the help of nuclear potentials (given analytically), as well as the KS potential v_s and the electron density of the respective atoms. Therefore, this model does not require the evaluation of integrals, originating from the Hartree repulsion V_H , demanding huge computational efforts.

Figs. 2–5 depict the binding curve, evaluated from Eq. (16), for the N_2 , CO, O_2 , and Be_2 , respectively. In the promolecular approach atomic fragments from ADF [79] have been employed. Atomic calculations were performed with zero spin polarization ($S = 0$) using the LDA Xonly functional and the QZ4P basis sets. The corresponding KS/LDA(Xonly)/QZ4P calculation for the N_2 , CO, O_2 , and Be_2 molecules were carried out for comparison. As can be seen from Figs. 2–5, the proposed fragment approach correctly predicts the occurrence of a chemical bond for dinitrogen, carbon monoxide, dioxygen, and diberyllium. According to the zeroth order model, N_2 is predicted to bind at 2.9 bohr with a dissociation energy of 0.843 hartrees, while CO, O_2 , and Be_2 bind at 3.0 bohr, 2.6 bohr, and 4.4 bohr with a dissociation energy of 0.758 hartrees, 1.049 hartrees, and 0.284 hartrees, respectively. Surely, the minimal positions of the binding curves from the zeroth order fragment approach do not equal the corresponding KS data exhibiting with a minimum at 2.1 bohr and -0.619 hartrees for N_2 , a minimum at 2.1 bohr and -0.551 hartrees for CO, a minimum at 2.3 bohr and -0.383 hartrees for O_2 , and a minimum at 4.7 bohr and -0.014 hartrees for Be_2 , respectively. However, notice the complexity

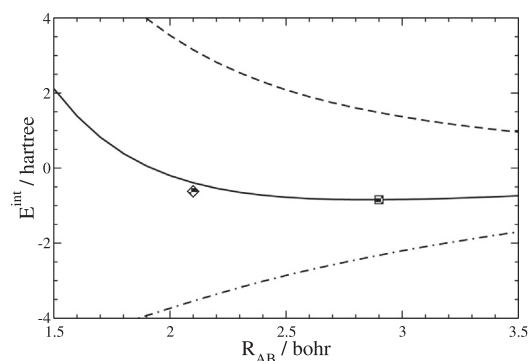


Fig. 2. Binding energy for the N_2 promolecule. The energy curve of the N_2 promolecule, shown by the solid line, exhibits a minimum at 2.9 bohr with a depth of -0.834 hartrees, marked by a square symbol. The corresponding KS data exhibits a minimum at 2.1 bohr and -0.619 hartrees, are marked by a diamond symbol. The kinetic energy of the promolecule is shown by the dashed line, while the potential energy is represented by the dash-dotted line.

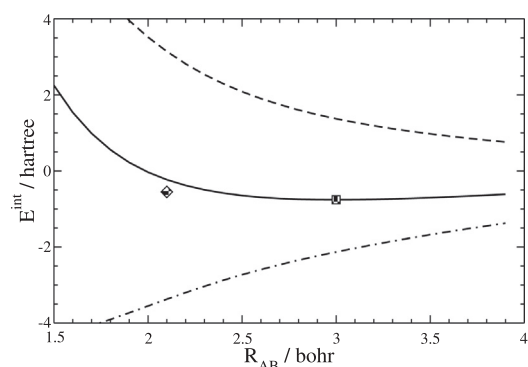


Fig. 3. Binding energy for the CO promolecule. The energy curve of the CO promolecule, shown by the solid line, exhibits a minimum at 3.0 bohr with a depth of -0.758 hartrees, marked by a square symbol. The corresponding KS data exhibits a minimum at 2.1 bohr and -0.551 hartrees, are marked by a diamond symbol. The kinetic energy of the promolecule is shown by the dashed line, while the potential energy is represented by the dash-dotted line.

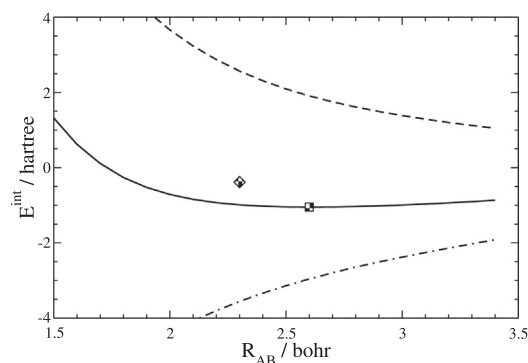


Fig. 4. Binding energy for the O_2 promolecule. The energy curve of the O_2 promolecule, shown by the solid line, exhibits a minimum at 2.6 bohr with a depth of -1.049 hartrees, marked by a square symbol. The corresponding KS data exhibits a minimum at 2.3 bohr and -0.383 hartrees, are marked by a diamond symbol. The kinetic energy of the promolecule is shown by the dashed line, while the potential energy is represented by the dash-dotted line.

of the given physical task as well as the fact that a simple model of frozen atomic fragments (that are not allowed to adapt) already captures the main characteristics of chemical bonding. The bonding minimum is obtained by a significant lowering of the potential energy (shown by the dash-dotted line), comprising the nuclear repulsion,

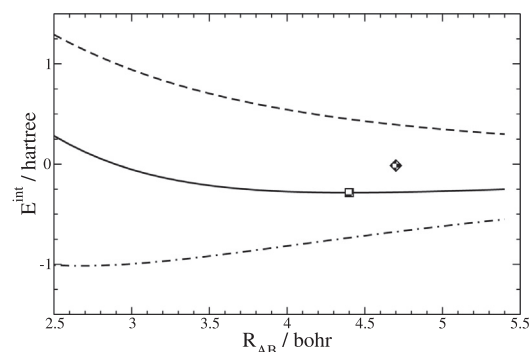


Fig. 5. Binding energy for the Be_2 promolecule. The energy curve of the Be_2 promolecule, shown by the solid line, exhibits a minimum at 4.4 bohr with a depth of -0.284 hartrees, marked by a square symbol. The corresponding KS data exhibits a minimum at 4.7 bohr and -0.014 hartrees, are marked by a diamond symbol. The kinetic energy of the promolecule is shown by the dashed line, while the potential energy is represented by the dash-dotted line.

electronic repulsion and electron-nuclear attraction, compensating for the increasing kinetic energy (shown by the dashed line), for decreasing internuclear distances. Since both repulsion terms are positive, the electron-nuclear attraction is the driving force for the formation of the chemical bond. In other words, in the picture proposed in this work, the chemical bond is due to significant energy lowering when the electrons of one atom feel the presence of the surrounding nuclear potentials.

5. Discussion

This work presents an orbital-free implementation of the original Hohenberg-Kohn density functional theory, that is able to predict bonding in molecules. The proposed method is completely parameter-free and does not require analytical ansatzes for the energy functionals. Instead, it is based on the idea that atoms are meaningful pieces of a molecule and thus, a promolecule serves as a good model for the latter. This idea is imposed on the physical equations, originating from density functional theory converted into a bifunctional formalism.

It has been shown that this form of density functional theory predicts bonding. Consequently, it should be possible to advance orbital-free chemical bonding concepts.

As for the numerical performance the proposed method offers a new route in the design of functionals. In the zeroth order fragment approach atomic Kohn-Sham potentials and respective densities can be optimized and tabulated for further treatment. The zeroth order fragment approach provides a meaningful chemical viewpoint (two atoms that attract each other) for the physical equations, that otherwise only treat attraction/repulsion between particles like electrons and nuclei. Advancing the zeroth-order fragment approach is in accord with the fundamental question of chemistry, whether or not two atoms bind together, now in a quantitative way. Assuming that the integrals appearing in the equation of the binding energy could be solved analytically, the description of the chemical bond would not require computational efforts. Instead, the chemical bond would be accessible in a simple manner from purely atomic quantities.

In addition, the proposed reformulation in terms of bifunctionals offers a systematic route in density functional approximations. Both terms, the kinetic energy and the electronic Coulomb repulsion, can be divided into a known functional part and a remainder. Surely, the known functional part can be treated exactly and only the remainder must still be approximated by the atomic fragment approach. This superior level of computation would allow for density adaptation in the promolecule.

Last but not least, the errors due to the fragment approximation might be corrected by a specific functional in addition to the electronic correlation. Surely, the very last step equals in complexity the initial

problem of density functional theory. However, the viewpoint proposed in this study offers a new and strategic way of subsequent approximations levels below the necessity of finding the Hohenberg-Kohn functional, whereby the zeroth order approximation has been shown to predict chemical bonding.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.comptc.2018.10.004>.

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