

Variational quantum Monte Carlo results for  $N_2$ ,  
 $N_2^+$  and  $C_2^-$  utilizing the four-dimensional density  
of Bright Wilson

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August 11, 2016

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## Abstract

Variational quantum Monte Carlo ground-state electron densities have first been obtained for  $\text{N}_2$  at its equilibrium bond length, as well for the isoelectronic ions  $\text{N}_2^+$  and  $\text{C}_2^-$  at the same bond length. These have been used to calculate the electrostatic potentials at the nucleus for all three species. Using the Bright Wilson four dimensional density, the ground-state energy has thus been reproduced. For  $\text{N}_2$ , also the Thomas-Fermi and the von Weizsäcker kinetic energies have been calculated.

Keywords: Homonuclear Diatomic Molecules; Electron Density; Quantum Monte Carlo; Inhomogeneous Electron Liquid.

# 1 Introduction

The electron density, namely the probability distribution of finding an electron at a given point in the space, is a fundamental quantity to understand, from a physico-chemical point of view, the behavior of the matter in any physical state [1]. Such a probability density has a clear quantum-mechanical interpretation and can be obtained either by the theory, from partial integration of the square of the electronic wave function, or by X-ray diffraction experiments, through the inverse Fourier transform of the structure factor [2]. For a molecular system, the electron density, which is normalized to the number of electrons, is mainly localized in regions which are both in close proximity of the nuclei and between the pairs of neighboring nuclei determining the size and the shape of the system itself. Despite the electron density is a function of only the position, it brings information on many-body effects. This fact has led to the development of the density functional theory (DFT) for the treatment of electronic systems in the ground state [3, 4] and of time-dependent DFT (TDDFT) to consider also the dynamics in the presence of a time-dependent external potential [5]. In this case the functional is the electronic energy that has been shown to be a functional of only the electron density [3] although, to date, its exact dependence remains unknown. However, the DFT has gained great popularity, as demonstrated by the huge number of publications still in fast growing [6].

In a more general sense, the theory of the electron density transcends the DFT being addressed to the fine study of all aspects related to the density function and not only to the search of an energy density functional. Noteworthy is, for example, the approach of Bader and co-workers based on gradient and Laplacian of the density [7] which is the basis of the so-called quantum theory of atoms in molecules (QTAIM) [8]. The study of electron localization from the electron density is also the basis of other derivations as done by Becke and Edgecombe for their electron localization function [9] or, as done very recently, to reconstruct a correlated wave function from the decomposition of Kohn-Sham orbitals [10].

In the context of the theory of electron density, we have been utilizing here the early important proposal of Bright Wilson [11] in which molecular ground-state energies for both neutral and charged species are represented in terms of their four

dimensional electron density  $\rho(x, y, z, Z)$  where (capital)  $Z$ , in atomic units, denotes a nuclear charge which can be chosen to be non-integer. To utilize the proposal in an optimal manner, we here invoke the variational quantum Monte Carlo (VMC) approach for the calculation of the above density. We prove the validity of Bright Wilson relation by accurate numerical examples on homonuclear diatomic molecules. Moreover, with the approximate but many body electron density computed here we calibrate a simple form of kinetic energy functional in an orbital free framework.

The paper is organized as follows. In Section 2, we give the computational details for the calculation of an efficient VMC wave function and of the relevant electron density function by means of a simple recipe. In Section 3, we apply the Bright Wilson formula to compute the ionization potential of  $N_2$  while, in Section 4, we use the electron density to evaluate the Thomas-Fermi (TF) and von Weizsäcker (W) kinetic energy functionals. Finally, conclusions are drawn in the last Section 5.

## 2 Computational details

The Bright Wilson formula for the energy of a molecule involves, in principle, the optimal electron density. For this reason, we resort in this work to a very efficient method of calculation of the wave function, namely the VMC method. The many-body VMC wave function used here was built in a standard Slater-Jastrow form of the type:

$$\Psi_{VMC}(\mathbf{r}_1, \mathbf{r}_2, \dots) = \Phi(\mathbf{r}_1, \mathbf{r}_2, \dots) \mathcal{J}(r_1, r_2, \dots, r_{12}, \dots) \quad (1)$$

where  $\Phi$  is written in term of a linear combination of Slater determinant products of spin-up and spin-down electrons as follows

$$\Phi = \sum_K D_K^\uparrow D_K^\downarrow d_K . \quad (2)$$

The determinants  $D_K^{(\sigma)}$  include occupied orbitals for all electrons resulting from a linear combination of Slater type atomic orbitals. To this purpose we use a basis set of 3 orbitals of 1s, 2s and 2p type for each atom. This choice introduces a good flexibility to the basis set without the need of an optimization of the atomic

orbital exponents. The full list of exponents used in this work is given in Table 1. The Jastrow factor  $\mathcal{J}$  is, instead, a function which depends explicitly on interparticle distances. In this work, we use a Jastrow factor that contains electron-nuclear, electron-electron, and electron-electron-nuclear terms[12]. The determinantal part of the wave function, instead, has been constructed by means of a recipe successfully used by Giannelli and Amovilli for the study of low lying states of NO molecule[13]. Following this recipe, the selection of the determinants is done in two steps: a first selection is performed from an extended CASSCF involving all the valence electrons by considering all excited configurations up to a given order of excitation with respect to the main configuration and, in the second step, by introducing a threshold on the determinant coefficients which allows the recovering of at least 97 percent of the resulting configuration interaction (CI) probability distribution. In this work we started from a CASSCF in which all the valence electrons are distributed in 10 active orbitals. Then, after a CI step including all excitations up to quadruples, we recovered more than 98 percent of the probability distribution by selecting the most important 33 determinants for  $C_2^-$  and  $N_2^+$  and 23 determinants for  $N_2$ . The coefficients of the determinants and the active orbitals have been reoptimized together with the Jastrow factor at the VMC step. For the optimization of all parameters in our SJ wave functions, we used the iterative linear method developed by Umrigar et al [14].

In order to apply the Bright Wilson relation for the electronic energy, one needs the computation of the electronic potential at all nuclear positions. Such a potential  $V_e$ , at a given coordinate  $\mathbf{r}_a$ , is calculated from the following relation in terms of the electron density  $\rho(\mathbf{r})$

$$V_e(\mathbf{r}_a) = - \int d\mathbf{r} \frac{\rho(\mathbf{r})}{|\mathbf{r}_a - \mathbf{r}|} \quad (3)$$

in atomic units. Because the density function used here, namely the number of electrons per unit volume, comes from the contraction (the integration over all the coordinates of  $N - 1$  electrons) of the square of the wave function, the electronic potential at the nuclear position can be computed directly from the Monte Carlo configurations sampled from the square of the VMC wave function itself. Thus, we

Z	$\zeta_{1s}$			$\zeta_{2s}$			$\zeta_{2p_x}$			$\zeta_{2p_y}$			$\zeta_{2p_z}$		
6.0	4.3	6.0	7.4	0.9	1.7	2.5	0.8	1.7	3.5	0.8	1.7	3.5	1.1	2.1	6.3
6.1	4.4	6.1	7.5	0.9	1.8	2.5	0.8	1.7	3.6	0.8	1.7	3.6	1.1	2.2	6.4
6.2	4.5	6.2	7.6	1.0	1.8	2.6	0.8	1.7	3.8	0.8	1.7	3.8	1.1	2.3	6.4
6.3	4.6	6.3	7.6	1.0	1.8	2.7	0.8	1.7	3.9	0.8	1.7	3.9	1.1	2.3	6.5
6.4	4.7	6.4	7.7	1.0	1.9	2.8	0.9	1.7	4.0	0.9	1.7	4.0	1.2	2.3	6.5
6.5	4.7	6.5	7.8	1.0	2.0	2.8	0.9	1.7	4.1	0.9	1.7	4.1	1.2	2.3	6.6
6.6	4.7	6.6	7.9	1.0	2.0	2.9	0.9	1.8	4.2	0.9	1.8	4.2	1.2	2.3	6.7
6.7	4.8	6.7	7.9	1.0	2.0	3.0	0.9	1.8	4.3	0.9	1.8	4.3	1.2	2.4	6.8
6.8	5.0	6.8	8.0	1.0	2.0	3.0	0.9	1.9	4.4	0.9	1.9	4.4	1.2	2.4	6.9
6.9	5.1	6.9	8.0	1.1	2.0	3.0	0.9	2.0	4.4	0.9	2.0	4.4	1.2	2.4	6.9
7.0	5.2	7.0	8.0	1.2	2.0	3.0	1.0	2.0	4.5	1.0	2.0	4.5	1.3	2.5	6.9

Table 1: Slater type orbital exponents used in this work. The molecular axis is the  $z$ -axis.

use the following average for the potential  $V_e(\mathbf{r}_a)$

$$V_e(\mathbf{r}_a) \approx -\frac{1}{M} \sum_{k=1}^M \sum_{j=1}^N \frac{1}{|\mathbf{r}_a - \mathbf{r}_j^{(k)}|} \quad (4)$$

where  $M$  is the number of sampled Monte Carlo configurations and  $N$  the number of electrons. As we will show below, the statistical error on this VMC estimate is small enough for our purposes in this work.

Although not used to compute the electrostatic potential at nuclei, we extracted an approximate electron density from our simulations. We performed this operation by means of an expansion of the density in terms of orthogonal functions generated by a symmetrical distribution of spherical gaussian functions along the molecular axis. Given a basis set  $\{\varphi_j(\mathbf{r})\}$ , if we write

$$\rho(\mathbf{r}) = \sum_j C_j \varphi_j(\mathbf{r}) \quad (5)$$

with the condition

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij} \quad (6)$$

we have

$$C_j = \int d\mathbf{r} \rho(\mathbf{r})\varphi_j(\mathbf{r}) \quad (7)$$

and, again, we can resort to a statistical average over the same sampled Monte Carlo configurations used above for the computation of the electrostatic potential at a given position. In this case we have

$$C_j \approx \frac{1}{M} \sum_{k=1}^M \sum_{j=1}^N \varphi(\mathbf{r}_j^{(k)}) . \quad (8)$$

We will use below this approximate electron density in the calculation of some orbital free kinetic energy density functionals.

Finally, to assess the quality of the VMC wave function, we performed some diffusion quantum Monte Carlo (DMC) calculations, using as trial wave function the VMC one, for the three different species  $C_2^-$ ,  $N_2^+$  and  $N_2$ . In this work, we used a time step of 0.0125 a.u.. A plot of the resulting VMC and DMC energy curves in proximity of the equilibrium internuclear distance is presented in Figure 1. The quality of our results is rather good (see, for comparison, refs [12, 16, 17]). For  $N_2$ , we recover about 87 percent of non relativistic correlation energy at VMC level and about 99 percent with DMC. Moreover, we tested also the DMC atomization energy of  $N_2$  by comparison with the nitrogen atomic energy resulting from an optimized guiding SJ wave function derived from a CASSCF(5,5) determinantal part. The resulting value, namely  $226.2 \pm 0.3$  kcal/mol, is in agreement within chemical accuracy with theoretical benchmark [18].

For the VMC optimization of the wave function and for the VMC and DMC energy calculations we used the CHAMP code [19].

### 3 Bright Wilson type calculation of ionization potential of $N_2$

In this work, we deal with homonuclear diatomic molecules. The electronic ground state energy, say  $E(N, Z)$ , is thus a function of the number of electrons  $N$  and of the

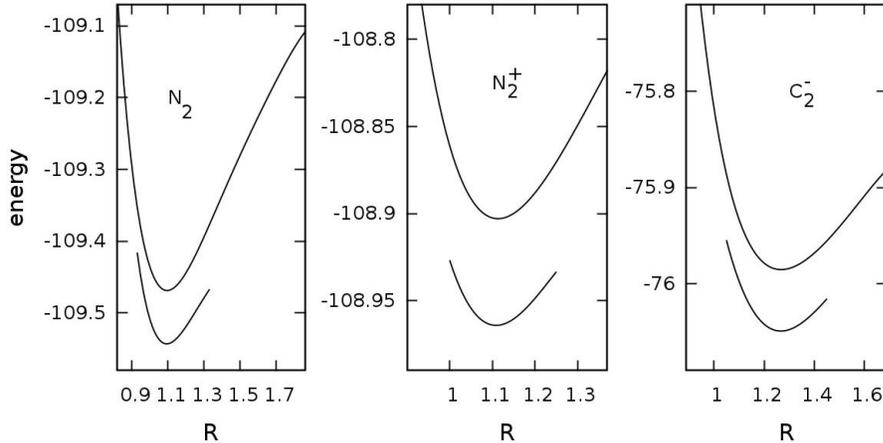


Figure 1: VMC (upper) and DMC (lower) energy curve as a function of the inter-nuclear distance ( $R$ ) for  $N_2$ ,  $N_2^+$  and  $C_2^-$  in proximity of the equilibrium distance. Energies are in Hartree and distances in  $\text{\AA}$ .

charge  $Ze$  of the two identical nuclei at a given fixed distance. The external nuclear potential  $v(\mathbf{r})$  is in a one-to-one correspondence with the electron density  $\rho(\mathbf{r})$  via the Hohenberg-Kohn theorem of density functional theory (DFT) [3] but a direct relation can be established by means of the Hellmann-Feynman theorem, namely

$$\left( \frac{\delta E}{\delta v(\mathbf{r})} \right)_N = \rho(\mathbf{r}) \quad (9)$$

which leads to the earlier formula of Bright Wilson [11], in atomic units,

$$E(N, Z) = \frac{Z^2}{R} - \int_0^Z dZ' \int d\mathbf{r} \left( \frac{1}{|\mathbf{r} - \mathbf{R}/2|} + \frac{1}{|\mathbf{r} + \mathbf{R}/2|} \right) \rho(\mathbf{r}, Z') \quad (10)$$

in which a four-dimensional electron density  $\rho(\mathbf{r}, Z')$  is explicitly considered. In this equation,  $Z'$  is a non integer nuclear charge introduced in order to define a charging process of the external potential. The above equation has been initially proposed for any polyatomic molecule [11] through a more general charging parameter ranging from 0 to 1, where 1 corresponds to the charging of all the nuclear

charges to their final values. The Bright Wilson relation is formally exact but, as we pointed out in our previous work on atoms [15], it is not possible to compute the electronic potential at nuclear position when one or more electrons cannot be bound. This normally happens when the nuclear charge is smaller than a critical value at which the ionization potential goes to zero. The Bright Wilson relation needs to be rewritten in the following form

$$E(N, Z) = E(N, Z_{cr}) + \frac{Z^2 - Z_{cr}^2}{R} - \int_{Z_{cr}}^Z dZ' \int d\mathbf{r} \left( \frac{1}{|\mathbf{r} - \mathbf{R}/2|} + \frac{1}{|\mathbf{r} + \mathbf{R}/2|} \right) \rho(\mathbf{r}, Z') \quad (11)$$

in practical applications on real systems. When  $Z = Z_{cr}$  we have  $E(N, Z_{cr}) = E(N - 1, Z_{cr})$  and we can use Eqn.(11) to get an explicit relation for the ionization potential, namely

$$IP(N, Z) = \int_{Z_{cr}}^Z dZ' \int d\mathbf{r} \left( \frac{1}{|\mathbf{r} - \mathbf{R}/2|} + \frac{1}{|\mathbf{r} + \mathbf{R}/2|} \right) [\rho^{(N)}(\mathbf{r}, Z') - \rho^{(N-1)}(\mathbf{r}, Z')] \quad (12)$$

which takes the simpler form

$$IP(N, Z) = 2 \int_{Z_{cr}}^Z dZ' [V_0(N, Z') - V_0(N - 1, Z')] \quad (13)$$

in terms of the electronic potential  $-V_0$  evaluated at the nuclear position ( $\pm\mathbf{R}/2$ ). Here, we use

$$V_0(N, Z) = \int d\mathbf{r} \frac{\rho^{(N)}(\mathbf{r}, Z)}{|\mathbf{r} - \mathbf{R}/2|} = \int d\mathbf{r} \frac{\rho^{(N)}(\mathbf{r}, Z)}{|\mathbf{r} + \mathbf{R}/2|}. \quad (14)$$

We have tested the ionization potential equation on nitrogen molecule at the equilibrium geometry. Our QMC energies together with the relevant  $V_0$  potential values are collected in Table 2 for  $N = 14$  and Table 3 for  $N = 13$ . The interval of nuclear charges considered in this study varies from  $Z = 6$  ( $\text{C}_2^-$ ) to  $Z = 7$  ( $\text{N}_2$  and  $\text{N}_2^+$ ). The statistical error on  $V_0$  resulted small enough to guarantee a satisfactory

$Z$	$E_{VMC}$	$V_0$	$E_{DMC}$
6.2	-82.0280(2)	18.957(2)	-82.1318(3)
6.3	-85.2489(2)	19.295(4)	-85.3501(2)
6.4	-88.5319(2)	19.666(1)	-88.6229(2)
6.5	-91.8745(2)	20.004(3)	-91.9677(3)
6.6	-95.2770(2)	20.348(3)	-95.3607(3)
6.7	-98.7377(2)	20.689(4)	-98.8186(3)
6.8	-102.2562(2)	21.025(2)	-102.3328(4)
6.9	-105.8321(2)	21.368(6)	-105.9100(3)
7.0	-109.4684(2)	21.691(3)	-109.5418(3)

Table 2: VMC electronic energy ( $E_{VMC}$ ) and electronic potential at nuclear position ( $V_0$ ) for a homonuclear diatomic molecule with 14 electrons and not integer nuclear charge  $Z$  in the  $^1\Sigma_g^+$  ground state. The internuclear distance is  $2.070 a_0$  (1.0954 Å), namely the equilibrium distance of  $N_2$  molecule. DMC electronic energy is also reported for comparison. All energies are in Hartree.

$Z$	$E_{VMC}$	$V_0$	$E_{DMC}$
6.0	-75.9287(2)	18.005(5)	-75.9940(2)
6.1	-78.9773(2)	18.331(5)	-79.0415(2)
6.2	-82.0816(2)	18.638(9)	-82.1578(2)
6.3	-85.2430(2)	18.989(2)	-85.3078(2)
6.4	-88.4595(2)	19.303(3)	-88.5226(2)
6.5	-91.7305(2)	19.629(5)	-91.7945(2)
6.6	-95.0576(2)	19.957(1)	-95.1198(2)
6.7	-98.4381(2)	20.266(8)	-98.5007(2)
6.8	-101.8723(2)	20.590(6)	-101.9346(2)
6.9	-105.3598(2)	20.917(4)	-105.4210(2)
7.0	-108.9020(2)	21.218(2)	-108.9624(2)

Table 3: VMC electronic energy ( $E_{VMC}$ ) and electronic potential at nuclear position ( $V_0$ ) for a homonuclear diatomic molecule with 13 electrons and not integer nuclear charge  $Z$  in the  $^2\Sigma_g^+$  ground state. The internuclear distance is  $2.070 a_0$  (1.0954 Å), namely the equilibrium distance of  $N_2$  molecule. DMC electronic energy is also reported for comparison. All energies are in Hartree.

interpolation with respect to  $Z$  for the reproduction, by integration over  $Z$  itself, of the Bright Wilson formula. As a result of this interpolation we have estimated the critical binding nuclear charge  $Z_{cr}$  by finding the value of 6.29 a.u. We remark here that this critical charge depends on the internuclear distance. For this reason,  $C_2^{2-}$  is not stable at the equilibrium distance of  $N_2$  while, in the repulsive region of the potential energy curve, it is more stable than  $C_2^-$  due to the electron affinity of the carbon atom.

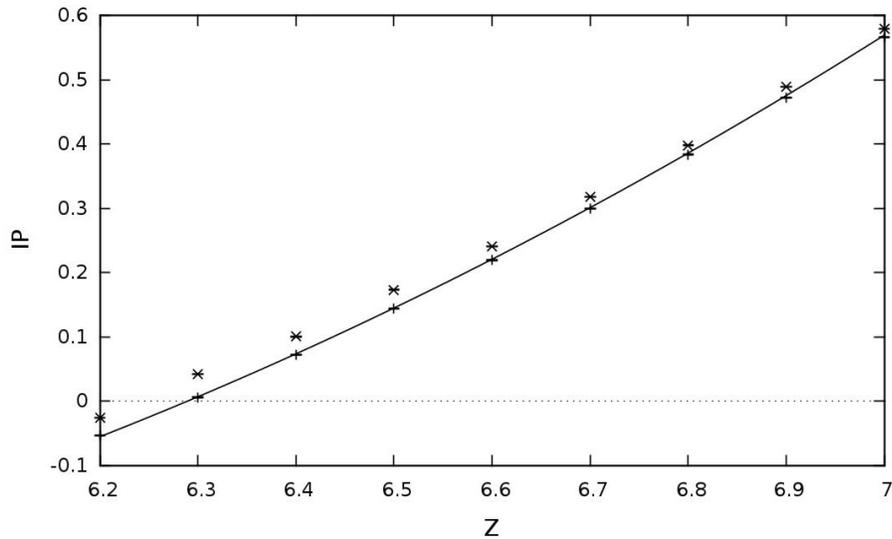


Figure 2: Comparison between the ionization potential (IP) derived from the Bright Wilson formula (line) and the computed VMC (+) and DMC (\*) corresponding values. All data are in a.u.

In Figure 2 we compare the ionization potential computed by means of the Bright Wilson formula with the corresponding VMC and DMC values resulting from QMC data of Tables 2 and 3. The agreement with VMC is very good and the discrepancies between the two sets of data, namely VMC and DMC, are between 0.01 and 0.02 Hartree.

## 4 Orbital free kinetic energy calculation

In Section 2, we have introduced a simple method for the estimate of the Bright Wilson four dimensional density from a set of QMC electronic configurations. Such a density function is subjected to a statistical error. It is important to remark that the method does not resort to any orbital based technique and could be useful in complementing with QMC the so called orbital free density functional theory (OFDFT)(see, for example, [20]). We have computed in this way the density for the cases with  $N = 14$  in the range of nuclear charges between  $Z = 6.2$  and  $Z = 7.0$ . In Figure 3, we show a comparison of the density contours calculated at these two extrema. The case with  $Z = 6.2$  is below the critical value, namely 6.29. The reduced confinement is evident from the shape of the contour lines.

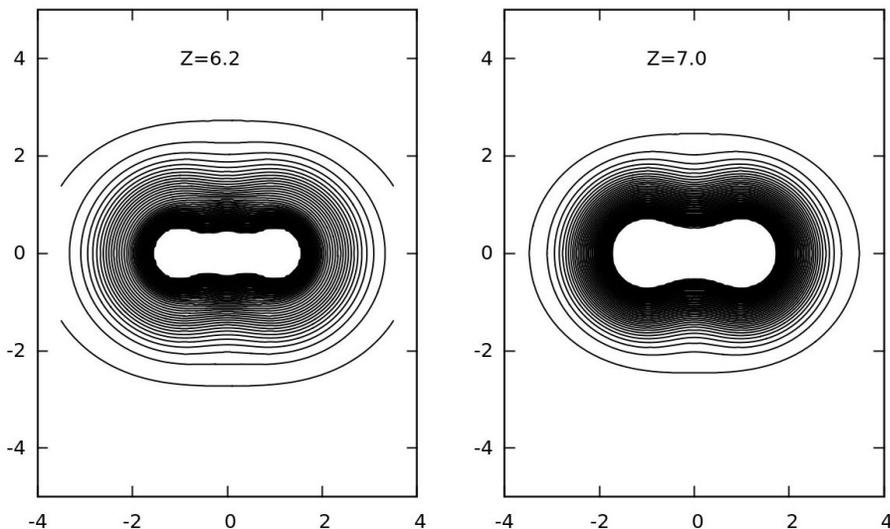


Figure 3: Electron density contour plots for the two limiting cases of homonuclear diatomic molecules with 14 electrons. All data are in a.u.

One of the main problem in OFDFT is the lack of a good functional for the kinetic energy. The forerunner of these functionals, namely the Thomas-Fermi one[21, 22], is valid only in the limit of a degenerate homogeneous electron gas. Moreover, it has been demonstrated that, with such a functional, it is not possible to form

molecules[23]. Inhomogeneity is of fundamental importance in forming chemical bonds. The von Weizsäcker kinetic energy functional[24], which depends explicitly on the gradient of the density, has been used to correct the Thomas-Fermi kinetic energy. In order to maintain the correct limit for the homogeneous electron gas, the corrected functional has the form

$$T_{TFW} = T_{TF} + \lambda T_W \quad (15)$$

where

$$T_{TF} = C_{TF} \int d\mathbf{r} \rho(\mathbf{r})^{5/3} \quad (C_{TF} = \frac{(3\pi^2)^{5/3}}{10\pi^2}) \quad (16)$$

and

$$T_W = \int d\mathbf{r} \frac{|\vec{\nabla}\rho|^2}{8\rho} . \quad (17)$$

The parameter  $\lambda$  has been found to be 1/9 by studying the inhomogeneity caused by a small perturbation due to a non constant external potential applied to the electron gas.

Here, to reproduce the density of all diatomic molecules with 14 electrons considered in this work, we used 33 spherical Gaussian functions distributed along the internuclear axis. We generated in this way 17 symmetrical orthogonal functions that have been combined to approximate the electron density by means of the average over the QMC configurations as described in Section 2. The statistical error on the coefficients determines at most an uncertainty on the kinetic energy functionals of the order

$$\Delta T \approx \langle T \rangle \sum_j \left| \frac{\Delta C_j}{C_j} \right| . \quad (18)$$

We report our computed TF and W kinetic energies in Table 4 together with the VMC corresponding values for both the Jackson-Feenberg (JF) and Pandharipande-Bethe (BT) forms. As expected, there is a big difference between the wave function based calculation of the kinetic energy and the other two density functionals. In the literature, there are few data of this type for N<sub>2</sub>. Here we mention the work of

Z	TF	W	JF	PB
6.2	74.60(11)	66.71(11)	82.74(2)	82.75(2)
6.3	77.35(12)	69.04(12)	85.89(3)	85.89(2)
6.4	80.40(12)	71.62(12)	89.02(2)	89.02(2)
6.5	83.37(13)	73.88(13)	92.30(3)	92.29(2)
6.6	86.27(14)	76.10(14)	95.59(2)	95.58(2)
6.7	89.55(14)	78.69(14)	99.00(4)	98.99(2)
6.8	92.82(15)	81.74(15)	102.39(2)	102.43(2)
6.9	96.12(16)	84.10(16)	105.89(2)	105.92(2)
7.0	99.56(16)	86.82(16)	109.45(2)	109.45(2)

Table 4: Comparison between Thomas-Fermi (TF) and von Weizsäcker (W) kinetic energy with VMC Jackson-Feenberg (JF) and Pandharipande-Bethe (BT) corresponding values for a homonuclear diatomic molecule with 14 electrons and not integer nuclear charge  $Z$  in the  $^1\Sigma_g^+$  ground state. The internuclear distance is  $2.070 a_0$  ( $1.0954 \text{ \AA}$ ), namely the equilibrium distance of  $\text{N}_2$  molecule. All energies are in Hartree. TF and W values have been calculated from a fitted density obtained from a set of VMC configurations.

Deb and Chattaraj [25] and of Piris and March [26]. Deb and Chattaraj found a TF energy of  $101.45 E_0$  and a W energy of  $85.62 E_0$  while Piris and March found a W energy of  $86.37 E_0$ . It is of some interest to make contact with the work of Piris and March who studied, in fact, dominantly the inhomogeneity W kinetic energy for some 30 homonuclear neutral diatomic molecules at their experimental geometries. They found that this W form varied simply with  $N^2$ ,  $N$  being the number of electrons.

Finally, we have attempted a fit of VMC kinetic energy by using the equation (15). Our best fit leads to a value of  $0.118(1)$  for  $\lambda$ , not very different from  $1/9$ . In Figure 4, we compare the resulting  $T_{TFW}$  from our fit with the VMC kinetic energy. The agreement is rather good and, although limited to the systems studied in this work, our scheme to connect QMC to OFDFT is promising for future development.

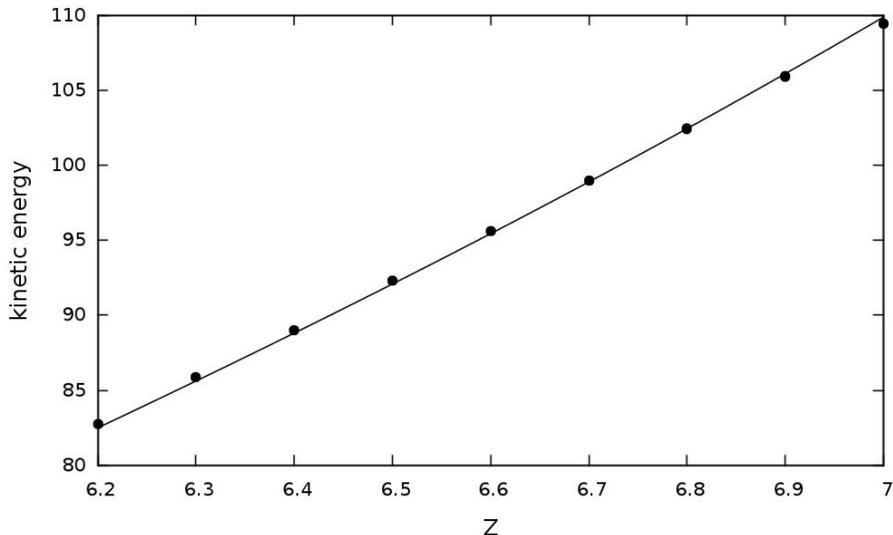


Figure 4: Thomas-Fermi-Weizsäcker kinetic energy calculated in this work (line) compared with the VMC kinetic energy (points) for some model homonuclear diatomic molecules with 14 electrons in the ground state.  $Z$  is the non integer nuclear charge in atomic units. The energy is in Hartree.

## 5 Conclusions

In this work, we have verified the formally exact formula of Bright Wilson for the electronic energy of a molecule on selected homonuclear diatomic systems. The formula involves a density function depending on four variables, namely the  $(x, y, z)$  coordinates of the point and a continuous charging parameter. Here, because we take homonuclear diatomic molecules, this parameter can be fixed directly to the charge of the nuclei. During the charging process, the nuclear charge is non integer. In order to consider the peculiarity of the Coulomb confinement, we have limited the charging process of the Bright Wilson formula to the interval of nuclear charges for which all electrons are bounded. As test example, we have considered the  $N_2$  molecule at the equilibrium distance. We computed a good correlated wave function at VMC level at different nuclear charges starting from 7 and reaching 6.2. In order to estimate the critical charge for which the ionization potential goes to 0, we did

the same for  $N_2^+$  at the same bond length of  $N_2$ . In this case we reduced the nuclear charge up to the limit of  $C_2^-$  ( $Z = 6$ ). We found a critical charge of 6.29. With this finding, we have been able to reproduce the VMC ionization potential, and consequently the VMC energy, of  $N_2$  by the use of the Bright Wilson formula.

As a further application, we used the approximate electron density generated by a relatively high number of VMC electronic configurations to compute the TF and the W kinetic energies for 14 electrons in the external field of two identical nuclei at a distance of  $2.070 a_0$  ( $1.0954 \text{ \AA}$ ), namely the equilibrium distance of  $N_2$ . We fitted the VMC kinetic energy by the form  $T_{TF} + \lambda T_W$  in the range of nuclear charges between 6.2 and 7. We found  $\lambda = 0.118 \pm 0.001$ , very close to  $\lambda = 1/9$ , the value typically used to correct the Thomas-Fermi kinetic energy for the inhomogeneity. We believe that this result, although limited to the selected systems studied in this work, is interesting and promising in the idea to establish a bridge between QMC and OFDFT for practical purposes.

### Acknowledgments

CA wishes to acknowledge financial support from the University of Pisa (Fondi di Ateneo and PRA\_2016\_46). NHM wishes to thank Professor Claudio Amovilli for inviting him to spend a period at the University of Pisa (I) and for most generous hospitality. NHM's contribution to the present work was largely completed during this stay in Pisa and brought to final fruition at DIPC (San Sebastian, E).

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