

Influence of electronic correlation in monoelectronic density in p-space

Beatriz Miguel · José M. García de la Vega

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Abstract The radial molecular monoelectronic density and their orbital contributions have been calculated in the momentum space. For these purposes, densities for the ground state of several atoms and molecules, using a cc-pVTZ basis set at HF level, as well as some post-HF and DFT methods are computed. The difference between the radial monoelectronic density computed with each method and that using the HF wave function is used as a tool to study the influence of the electronic correlation in the momentum space. Densities obtained with post HF calculations show a similar behavior around $p = 1.0$ and 2.0 , that are different from the DFT results. Radial momentum densities (p-densities) are more influenced by the electronic correlation than the exchange part of the DFT methods. CISD p-density is more affected than DFT p-density when the intermolecular distance increases. An analysis of the powers of moments calculated with different methods has been carried out.

Keywords Radial momentum density · Momentum space · Addition rule

1 Introduction

The Schrödinger equation in momentum space (p-space) has interest as a source of new information [1]. The solution of this equation in p-space can proceed along two paths which have in common the use of the Fourier Transform method. Thus, one can perform the transformation of the equation and try and solve it. Alternatively, one can obtain directly the transforms of the function in position space and use the resulting functions in p-space in this evaluation.

The electron momentum density (p-density) is complementary to the usual position density (r-density) perspective. For this reason, some additional information can be exploited from p-density. The renewed efforts in the study of the representation are due to the interest in the calculation of expectation values, associated with physical observables, as well as other momentum-related properties [2,3] and which can now be measured with modern experimental techniques, namely: X-ray experiments, Compton collisions with γ -ray, electron collisions at high energies and spectroscopy (e, 2e) [4,5]. Compton scattering experiments can be used to measure spherically averaged momentum densities for molecules. The spherically averaged momentum densities remain of interest because they are relevant for the gas phase, where the molecule is freely rotating. Recently, Thakkar [6,7] has published two excellent reviews, about the state of art of electron momentum density.

Electron momentum spectroscopy, providing direct information on the electron momentum density distribution, has confirmed the importance and, consequently, the need for a knowledge of the density distribution in both the highest occupied and the lowest unoccupied molecular orbitals, as a source of more useful information than that obtained from the total density distribution. The knowledge of the electron momentum distribution, which includes a realistic allowance

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B. Miguel (✉)
Departamento Ingeniería Química y Ambiental,
Universidad Politécnica de Cartagena,
Paseo Alfonso XIII 44, 30203 Cartagena, Spain
e-mail: beatriz.miguel@upct.es

J. M. García de la Vega
Departamento de Química Física Aplicada, Facultad de Ciencias,
Universidad Autónoma de Madrid, 28049 Madrid, Spain
e-mail: garcia.delavega@uam.es

of electron correlation, can be of particular importance when formulating density functional analysis.

Banyard et al. [8–12] analyzed correlation effects in p-space for some states of He and for Li atoms, and also for doubly excited systems and some excited states of He-like ions using configuration interaction (CI) wavefunctions. They proved to be particularly informative regarding the interplay between the angular and radial components of electron correlation. The interest of this observation is to introduce correlation specific regions of space to build an effective set of basis functions in future CI calculations. Effects of electron correlation in p-space for HeH⁺ was studied by Reed and Banyard [13, 14]. They studied the momentum distribution for this two-electron system as a function of the internuclear distance. They found that the Coulomb hole for this system in p-space is very similar to that obtained for He atom and that correlation removes charge from the bond region.

Sarsa et al. reported correlated results of single electron properties for the He to Ne atoms [15, 16] and for the atomic beryllium isoelectronic series [17] using Monte Carlo technique. They studied the correlation effects in p-space using an extensive set of correlated functions. They obtained p-space properties for atoms that can be considered as “exact”. Moreover, they found the lack of a monotonic convergence for some atomic properties and they concluded that the electron correlation does not present a systematic effect on the momentum distribution.

In spite of the importance of powers of moments, because they are related with physical properties, few papers have been published devoted to these calculations in molecules [18–24]. Moreover, we can calculate directly the powers of momentum expectation from the molecular mono-electronic density.

The purpose of this paper is to give the mathematical tools to evaluate molecular mono-electronic densities from a density matrix obtained in a molecular standard calculation with a Gaussian basis set. We have not considered the effect of the basis set, due to there are not “exact” available results for molecules. Then we present the results of these densities for several atoms and molecules computed with different levels post-HF and DFT methods. From these results, we analyze the effect of electron correlation in the radial mono-electronic p-density depending on the kind of method employed. We also study the influence of electron correlation as a function of the internuclear distance and finally we compare the power of calculated moments with the “best estimates” proposed recently for molecules [24].

2 Molecular mono-electronic densities

The mono-electronic density in the p space for an N electron system

$$\gamma(p) = \int |\Psi(\mathbf{p}_1 \mathbf{p}_2 \mathbf{p}_3 \dots \mathbf{p}_N)|^2 d\mathbf{p}_2 d\mathbf{p}_3 \dots d\mathbf{p}_N d\Omega_{\mathbf{p}_1} \quad (1)$$

$d\Omega_{\mathbf{p}_1}$ being the angular differential for $\mathbf{p}_1 = (p_1, \theta_{p_1}, \phi_{p_1})$. In the case of a monodeterminantal function, Eq. 1, could be written as a lineal combination of the orbital contributions, $\gamma_{jj}(p)$:

$$\begin{aligned} \gamma(p) &= \sum_{j=1}^N \gamma_{jj}(p) \\ &= \sum_{j=1}^N \int \Phi_j^*(\mathbf{p}) \Phi_j(\mathbf{p}) d\Omega_p \end{aligned} \quad (2)$$

The approximation of lineal combination of atomic orbitals (LCAO) is usually used in the calculations of the molecular electronic structure and the molecular spinorbitals are expressed by a lineal combination of a non complete basis set functions $\{\varphi_i\}_{i=1}^m$, that is

$$\Phi_j(\mathbf{p}) = \Phi_j(p, \theta_p, \phi_p) = \sum_{s=1}^m c_{sj} \varphi_s(p, \theta_p, \phi_p) \quad (3)$$

Following this approximation the orbital contributions to the molecular mono-electronic density, defined by Eq. 2 could be rewritten as

$$\gamma_{jj}(p) = \sum_{r,s}^m c_{rj}^* c_{sj} \int \varphi_r^*(\mathbf{p}) \varphi_s(\mathbf{p}) d\Omega_p \quad (4)$$

Kaijser and Smith [25] demonstrated that the Fourier Transform of a Gaussian type orbital (GTO), when $n = l + 1$, is given by:

$$\begin{aligned} \widehat{\varphi}_{n,l}^m(p, \theta_p, \phi_p) &= (-i)^l \frac{B(n, \alpha)}{(2\alpha)^{(n+1/2)}} e^{-i\mathbf{p}\mathbf{A}} p^{(n-1)} e^{-\frac{p^2}{4\alpha}} \\ &\quad \times Z_{l,m}(\theta_p, \phi_p) \end{aligned} \quad (5)$$

\mathbf{A} being the position vector of the nuclei where the studied function $\varphi(\mathbf{r})$ is centered in the molecular system, so \mathbf{r}_i is defined as $\mathbf{r}_i = \mathbf{r} - \mathbf{A}$. $B(n, \alpha)$ and $Z_{l,m}(\theta_p, \phi_p)$ are the normalization constant and the real spherical harmonics, respectively, both defined elsewhere [23].

The use of cartesian GTO's in the molecular calculations implies that the $l - 2$ (for $l \geq 2$) and $l - 4$ (for $l \geq 4$) components are also required in the p-space [23].

Using the LCAO and a GTO's basis set, the orbital contribution to the mono-electronic density is written as

$$\begin{aligned} \gamma_{jj}(p) &= \sum_r^m \sum_s^r \left(c_{rj}^* c_{sj} \int \varphi_r^*(\mathbf{p}_A) \varphi_s(\mathbf{p}_B) d\Omega_p \right. \\ &\quad \left. + c_{rj} c_{sj}^* \int \varphi_s^*(\mathbf{p}_A) \varphi_r(\mathbf{p}_B) d\Omega_p \right) \end{aligned} \quad (6)$$

\mathbf{p}_A and \mathbf{p}_B being the vectors of the electron momenta represented by the functions $\varphi_r^*(\mathbf{p}_A)$ and $\varphi_s(\mathbf{p}_B)$. Considering the GTO Fourier transform definition, Eq. 5, in the expression $\varphi_r^*(\mathbf{p}_A)\varphi_s(\mathbf{p}_B) + \varphi_s^*(\mathbf{p}_A)\varphi_r(\mathbf{p}_B)$ the following expression is produced

$$(i)^{l_r} (-i)^{l_s} e^{-i\mathbf{p}\mathbf{C}} + (-i)^{l_r} (i)^{l_s} e^{i\mathbf{p}\mathbf{C}} \\ = 2(-1)^v \begin{cases} \cos(\mathbf{p}\mathbf{C}) & \text{if } \mu = 0 \\ \sin(\mathbf{p}\mathbf{C}) & \text{if } \mu = 1 \end{cases}$$

with $l_s - l_r = 2v - \mu$, \mathbf{A} and \mathbf{B} being the position vectors of the nuclei where $\hat{\varphi}_{n_r, l_r}^{m_r}$ and $\hat{\varphi}_{n_s, l_s}^{m_s}$ are centered, defining $\mathbf{C} = \mathbf{A} - \mathbf{B}$, C as the modulus of \mathbf{C} .

Rewritten Eq. 6

$$\gamma_{jj}(p) = \sum_r^m \sum_{s=1}^r c_{rj}^* c_{sj} \frac{B(n_r, \alpha_r) B(n_s, \alpha_s)}{(2\alpha_r)^{n_r+1/2} (2\alpha_s)^{n_s+1/2}} p^{n_r+n_s-2} \\ \times e^{-p^2/\alpha} \int Z_{l_r, m_r}(\Omega_p) Z_{l_s, m_s}(\Omega_p) 2(-1)^v \\ \times \begin{cases} \cos(\mathbf{p}\mathbf{C}) & \text{if } \mu = 0 \\ \sin(\mathbf{p}\mathbf{C}) & \text{if } \mu = 1 \end{cases} d\Omega_p \quad (7)$$

where $\alpha = (4\alpha_r \alpha_s)/(\alpha_r + \alpha_s)$.

The density matrix describes the degree to which individual basis functions contribute to the many electron wave function, and thus, how energetically important the Coulomb and exchange integrals should be. The elements of this density matrix, P , are computed as:

$$P_{\lambda\sigma} = 2 \sum_i^N a_{\lambda i} a_{\sigma i} \quad (8)$$

where the coefficients $a_{\lambda i}$ specify the normalized contribution of a basis function σ to the molecular orbital i .

So Eq. 4 could be rewritten as

$$\gamma_{jj}(p) = \sum_{r,s}^m a_{rj}^* a_{sj} \int \varphi_r^*(\mathbf{p}) \varphi_s(\mathbf{p}) d\Omega_p \quad (9)$$

The powers of the momentum expectation values are also obtained from this monoelectronic density:

$$\langle p^n \rangle = \int_0^\infty p^n \gamma_{jj}(p) dp \quad (10)$$

3 Results and discussion

In the theoretical study of the photon collisions with molecules, the molecular Compton profiles, that are computed from the direct integration of the monoelectronic density in the p space, are usually estimated from the sum of the atomic Compton profiles of the atoms building the molecule under consideration. This treatment is known as the addition rule

[26–29]. However, in several works Bader [30] has demonstrated how the variations of the molecular electronic density in the r space, with respect to the sum of the atomic electronic densities of atoms forming the molecule, allow to describe and characterize the chemical bond. So, it could be expected that the electronic density in the momentum space behaves in a similar way, and it will be preferable to compute the electronic densities and the Compton profiles directly from the molecular wavefunction in the p -space. In other words, the contribution to the electron density in the p -space due to the formation of a chemical binding is lost when the addition rule is employed.

We have computed the molecular radial monoelectronic densities as well as the orbital contributions. In Fig. 1, the radial orbital monoelectronic densities for water molecule are plotted. These values have been computed using the monodeterminantal molecular wavefunction obtained with the Hartree Fock (HF) wavefunction and using cc-pVTZ basis set [31]. The radial molecular monoelectronic density and its orbital contributions are smooth functions (see top Fig. 1). We have also calculated the atomic monoelectronic density for oxygen and hydrogen atoms. The approximate electronic p -density of water has been calculated applying the addition rule, using the corresponding atomic densities, for comparing these results with the density computed directly with the molecular wavefunction. The difference between both electronic p -densities of water is presented in Fig. 1 (bottom). This difference plot shows changes of 1.5 au in the molecular density for p around 0.5 and of 1.0 for p around 1.3, showing that the addition rule approximation, underestimates the molecular density for $p \leq 1.0$ and overestimates it for $1.0 < p \leq 2.0$, approximately.

One important aspect to be taken into account in the molecular calculations is the influence of the electronic correlation in the evaluation of a molecular property. For this reason, we have performed some post-HF calculations with the cc-pVTZ basis set. Two post-HF calculations have been carried out, namely a Moller-Plesset [32] approximation of second order (MP2), a CI calculation with single and double excitations [33,34] (CISD), and four Density Functional Theory (DFT) calculations using Becke [35] and Slater [36] exchange functionals, and LYP [37] and VWN [38] correlation functionals.

Some authors [9,39] have shown that the differences between electron-pair intracule densities in the p -space computed at HF and FCI levels show the well-known Coulomb hole in the ground state of the He atom. A physical picture of the electronic correlation effects is usually given by the plot of the Coulomb hole defined [40] as the difference between the accurate and the HF intracule densities. In a similar way, the differences between the density obtained from correlated wavefunctions and that obtained with not correlated wavefunctions shows the non-dynamical correlation contribution to the monoelectronic density as a function of the

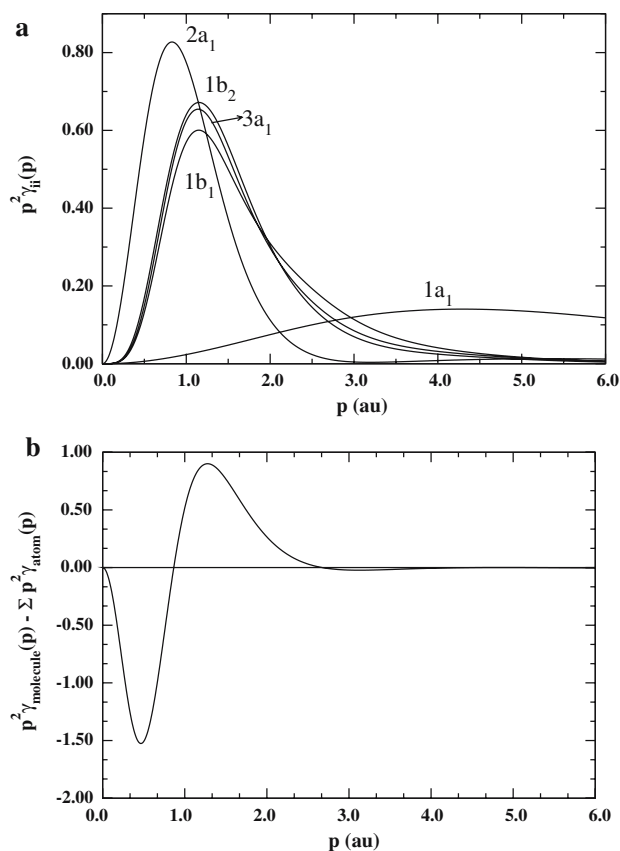


Fig. 1 Orbital radial mono-electronic densities (*top*) for the water molecule, at HF/cc-pVTZ level. Difference between computed total radial mono-electronic density and the value obtained applying the addition rule (*bottom*)

inter-electronic momentum coordinate. In order to study these correlation effects in the mono-electronic density we define in a similar way:

$$\Delta\gamma(p) = \gamma(p) - \gamma_{\text{HF}}(p) \quad (11)$$

As a test, we have chosen Ne atom, and five molecules: methane, acetaldehyde, carbon tetrafluoride, ethylene and cyanogen. In all cases, the singlet ground state in the experimental geometry has been computed. Differences between radial mono-electronic densities at post-HF and DFT levels with respect to HF level are represented in Fig. 2.

In general, all radial mono-electronic densities computed with correlation densities matrices show a similar behavior, but CISD and MP2 densities give results nearest to the HF, otherwise DFT methods present a higher difference in the p -density with respect to that the HF p -density. The Slater exchange functional gives the lowest minimum and the highest maximum. All the curves obtained with the post-HF density matrices show a minimum around $p = 1.0$ – 2.0 , and a maximum around $p \leq 1.0$. Density differences for the four DFT methods show a similar behavior in these six systems, with a maximum that is higher and a minimum that

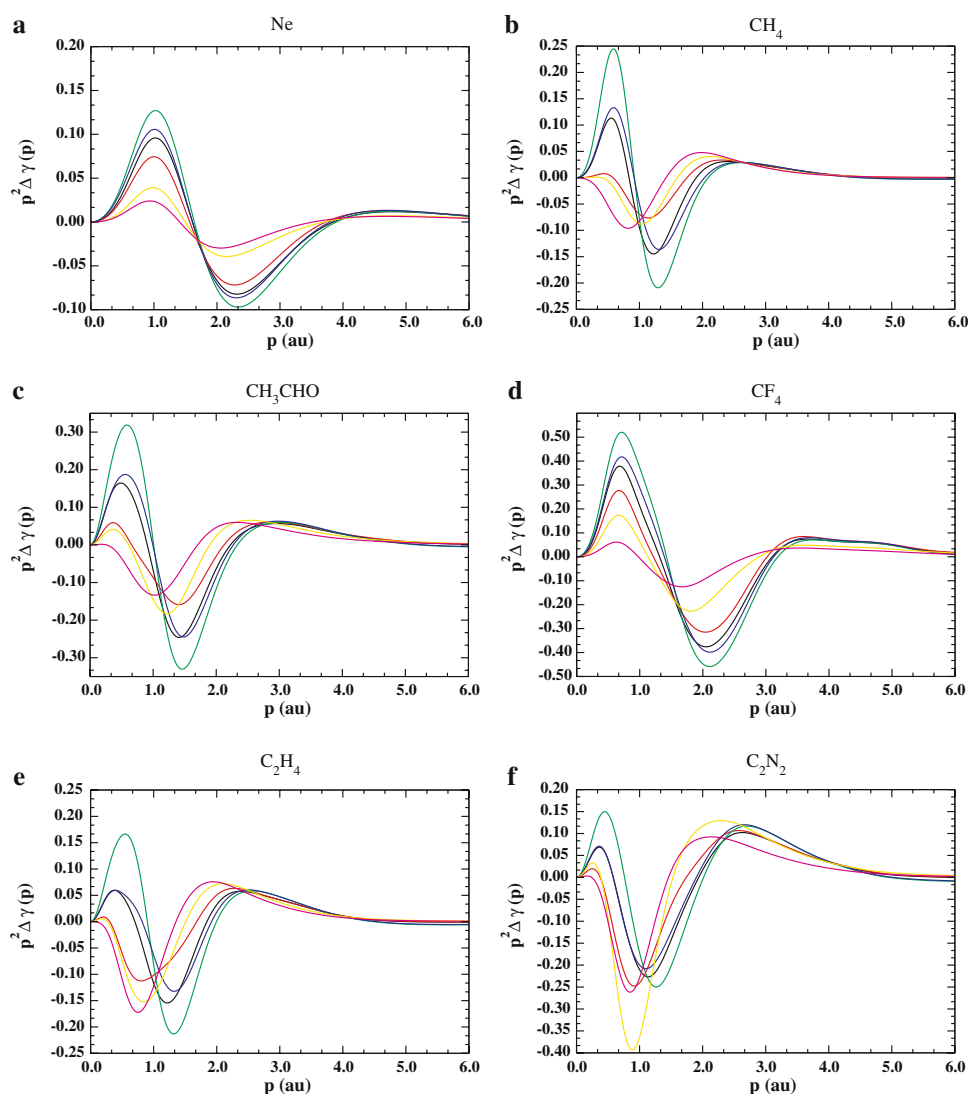
is lower than those obtained with MP2 and CISD methods. Moreover, SLYP functional always gives the major difference. The shape of those curves for MP2 and CISD method is quite different for the six systems, showing in some cases a translation of minima and maxima with the values obtained with respect to DFT methods. The behavior of BVWN functional is very similar to that of MP2 method (see Fig. 2). The position of maxima and minima are equivalent and the values of $p^2 \Delta\gamma(p)$ are the same.

In order to carry out a deeper study of the behavior of the $p^2 \Delta\gamma(p)$ for postHF and DFT methods, we have computed the water molecule. We use the same basis set (cc-pVTZ), but we have included MP2, MP3, MP4, CID, QCISD and CCD, as post-HF methods and eleven DFT methods, the three above considered DFT methods plus other eight functionals, namely: BP86, SPW91, LSDA, SP86, BPW91, X α LYP, X α VWN and X α PW91. These differences for the radial mono-electronic densities computed with the post HF water densities are represented in Fig. 3. To get an easier visualization, the 14 selected methods are depicted into two separated graphics in Fig. 3. The six post-HF and the eleven DFT curves are represented at the top and the bottom of Fig. 3, respectively.

The main features of the representation of Fig. 3 are that the position of the maxima and the minima corresponding to DFT methods which are located in the same points ($p = 0.7$) and ($p = 1.7$), respectively, and with higher values of $p^2 \Delta\gamma(p)$ than those obtained with post HF methods. Functionals with Slater exchange (SLYP and SVWN) show higher differences than when Becke exchange (BLYP and SVWN) is used and they are independent from the correlation functional employed. MP3, MP4, CCD and QCISD methods show their minima at $p = 1.3$ and their maxima at $p = 0.5$, and with values of $p^2 \Delta\gamma(p)$ very small. However, CISD only shows a minimum to shorter p and MP2 shows a higher maximum and lower minimum with a positive displacement of p .

We have considered the influence of the molecular geometry on the variation of $p^2 \Delta\gamma(p)$. For this purpose, two diatomic molecules (one homonuclear, F₂, and another heteronuclear, HF) have been selected. In Fig. 4, the variation of the radial mono-electronic density with the internuclear distance at BLYP and CISD levels, with respect to HF level, is shown. Taking into account the above obtained experience from Fig. 2, we have chosen two methods that have presented great differences in the radial mono-electronic density systems here studied, that is CISD and BLYP. At the equilibrium distance (F₂ 1.42 Å and HF 0.96 Å), the shape of the curves is very similar in both molecules (see solid and dashed red lines in Fig. 3). Maxima and minima appear around $p = 0.8$ and $p = 2.0$, respectively. In both molecules, BLYP method is less sensitive to the distance, maintaining the position of maxima and minima in the same value of p for bond distances larger and shorter (see blue and black lines in Fig. 3).

Fig. 2 Differences of radial mono-electronic densities for some systems: Ne atom, methane, acetaldehyde, carbon tetrafluoride, ethylene and cyanogen, using cc-pVTZ basis set and several methods of calculation: BLYP (black line), BVWN (red line), SLYP (green line), SVWN (blue line), MP2 (yellow dash line) and CISD (magenta line)



Nevertheless, the shape of $p^2 \Delta\gamma(p)$ curves is different for CISD method, particularly for larger distances in F_2 . At distances shorter than 1.5 \AA the BLYP wavefunction gives description of the radial mono-electronic density which is rather different from that obtained with CISD wavefunction, with respect to HF wavefunction. However, for both molecules at $R=2.0 \text{ \AA}$, the density description of the CISD wavefunction differs more than HF density.

From Eq. 10, the power of p can be calculated from the mono-electronic density. These values are another test to study the influence of correlation energy on the p -density. For this reason, we have decided to compute the powers of moments for the set of the eight molecules (hydrium fluorine, fluorine, water, methane, ethylene, acetaldehyde, cyanogen and carbon tetrafluoride) with the addition of He and Ne atoms. We show in Table 1, the powers of moments from $n = -2$ to 4 for these ten systems at HF, MP2 and CISD levels and in Table 2, at DFT levels (BLYP, BVWN, SLYP and SVWN).

In the last column of Table 1, we have referenced the best estimate molecular values [24] to compare them with the evaluated powers in this paper. Moreover, we have added, as reference values, the “exact” atomic ones [16] ($n = -2$ to 2) for He and Ne atoms.

From the inspection of Tables 1 and 2, we obtain some trends in the behavior of powers of moments depending on the kind of method including correlation. Some of them agree with the results previously obtained by Hart and Thakkar [24] for a large number of molecules. Comparing post-HF and DFT values of Tables 1 and 2 with the corresponding HF value, we observe that for n negative, in general, the corresponding value with post-HF methods (MP2 or CISD) are lower than those obtained with HF method, and for n positive the post-HF values are higher than those obtained with the HF method. Moreover, for n positive the corresponding MP2 and CISD values are very similar. This conclusion is in agreement with Hart and Thakkar, when they wrote that MP2

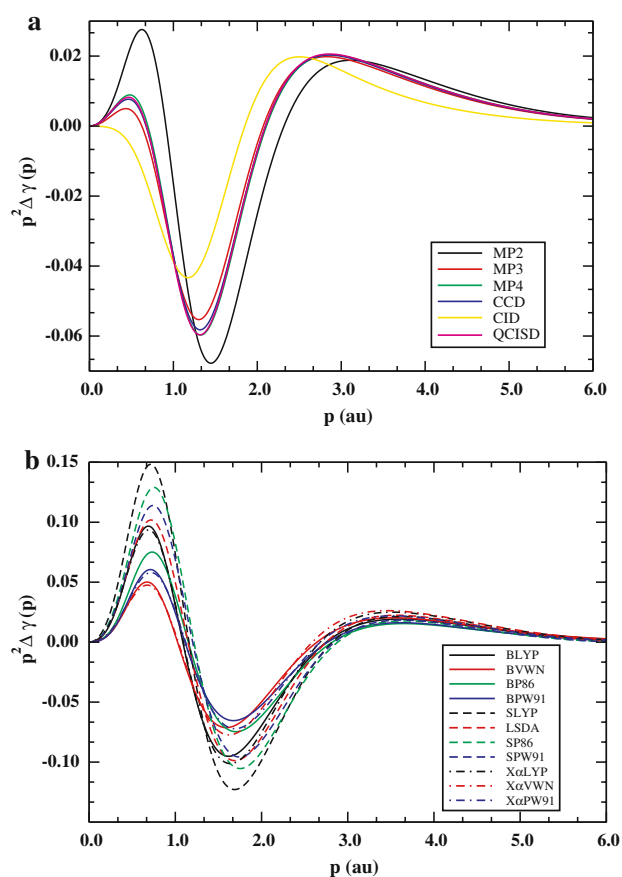


Fig. 3 Differences of radial mono-electronic densities for water molecule, using several methods of calculation and cc-pVTZ basis set. *Top* post HF methods: MP2, MP3, MP4, QCISD, CID and CCD. *Bottom* DFT methods: BLYP, BVWN, BP86, SPW91, SLYP, LSDA, SP86, BPW91, X α LYP, X α VWN and X α PW91

method works well for n positive. Comparing DFT values with HF values, we can conclude that for n negative DFT values are higher than the corresponding HF ones, and for n positive DFT values are smaller than HF ones. Moreover, for n negative BLYP and BVWN values are lower than SLYP and SVWN ones. The reverse behavior is found for n positive, showing the influence of the exchange *vs* the correlation as we have observed above for $p^2 \Delta\gamma(p)$. Finally, comparing the results here obtained with the best estimates for molecules, we can see that for n negative CISD and SLYP values are more similar to those computed in Ref. [24], whereas for n positive the best estimate values are closer than MP2 and BVWN computed values. Clearly, these results agree with the third conclusion of Hart and Thakkar about the bad description given by KS density matrix for the calculation of those powers of moments. The comparison of the results here obtained for He and Ne atoms with “exact” ones [16] cannot be done directly, because a percentage of the electronic correlation is due to the Gaussian basis sets used. It is

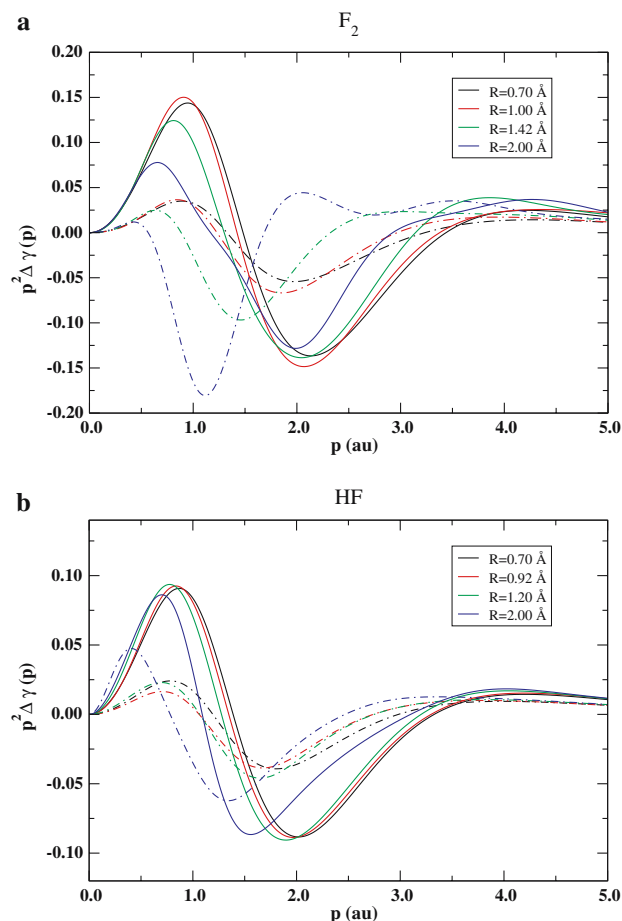


Fig. 4 Differences of radial mono-electronic densities for fluorine (*top*) and hydrium fluorine (*bottom*) molecules at different internuclear distances. *Solid* and *dashed* lines correspond to BLYP and CISD calculations, respectively

remarkable that the powers here obtained for $n = 4$ present, in some cases, values that are lower than the best estimates.

4 Concluding remarks

The molecular p -density for water molecule computed from atomic contributions and using the addition rule underestimates the computed molecular values for lowest p values, overestimates it for medium values ($1 \leq p \leq 2$) and give accurate results at high values.

We have proposed the function $p^2 \Delta\gamma(p)$ as a test of the effect of the correlation in the mono-electronic density. This function shows that the HF wavefunction gives the poorest description at lowest momenta, as long as the covalent character of the bond decreases, if compared with DFT or MP2 or CISD densities. These values are obtained in the eight molecular systems presented in this paper. However, if compared to the HF results in absolute value, the DFT densities

Table 1 $\langle p^n \rangle$ Moment values using HF and post-HF methods

| | | HF | MP2 | CISD | Ref. [24] |
|----------|-------------------------------|--------------|--------------|--------------|---------------------------|
| $n = -2$ | He | 0.40142(+01) | 0.40100(+01) | 0.40167(+01) | 0.4096(+01) ^a |
| | Ne | 0.53228(+01) | 0.53677(+01) | 0.53526(+01) | 0.5634(+01) ^a |
| | HF | 0.75037(+01) | 0.75768(+01) | 0.75710(+01) | 0.76291(+01) |
| | F ₂ | 0.11429(+02) | 0.11416(+02) | 0.11363(+02) | 0.11894(+02) |
| | H ₂ O | 0.10564(+02) | 0.10683(+02) | 0.10672(+02) | 0.10285(+02) |
| | CH ₄ | 0.17773(+02) | 0.17775(+02) | 0.17672(+02) | 0.17522(+02) |
| | C ₂ H ₄ | 0.24765(+02) | 0.25012(+02) | 0.24734(+02) | 0.25653(+02) |
| | CH ₃ COH | 0.30663(+02) | 0.31502(+02) | 0.30891(+02) | 0.30802(+02) |
| | C ₂ N ₂ | 0.28844(+02) | 0.29368(+02) | 0.28951(+02) | 0.29557(+02) |
| | CF ₄ | 0.27309(+02) | 0.27590(+02) | 0.27419(+02) | 0.27771(+02) |
| $n = -1$ | He | 0.21311(+01) | 0.21278(+01) | 0.21286(+01) | 0.2138(+01) ^a |
| | Ne | 0.54124(+01) | 0.54294(+01) | 0.54213(+01) | 0.5515(+01) ^a |
| | HF | 0.64025(+01) | 0.64165(+01) | 0.64096(+01) | 0.64750(+01) |
| | F ₂ | 0.10220(+02) | 0.10206(+02) | 0.10199(+02) | 0.10741(+02) |
| | H ₂ O | 0.75212(+01) | 0.75201(+01) | 0.75052(+01) | 0.75845(+01) |
| | CH ₄ | 0.10092(+02) | 0.10057(+02) | 0.10027(+02) | 0.10000(+02) |
| | C ₂ H ₄ | 0.14997(+02) | 0.14909(+02) | 0.14882(+02) | 0.14889(+02) |
| | CH ₃ COH | 0.19820(+02) | 0.19793(+02) | 0.19744(+02) | 0.19783(+02) |
| | C ₂ N ₂ | 0.20082(+02) | 0.19919(+02) | 0.19938(+02) | 0.20014(+02) |
| | CF ₄ | 0.25205(+02) | 0.25279(+02) | 0.25210(+02) | 0.25328(+02) |
| $n = 1$ | He | 0.28001(+01) | 0.28123(+01) | 0.28145(+01) | 0.282(+01) ^a |
| | Ne | 0.35215(+02) | 0.35246(+02) | 0.35258(+02) | 0.35(+02) ^a |
| | HF | 0.30405(+02) | 0.30469(+02) | 0.30473(+02) | 0.30438(+01) |
| | F ₂ | 0.59661(+02) | 0.59674(+02) | 0.59563(+02) | 0.58572(+02) |
| | H ₂ O | 0.26052(+02) | 0.26148(+02) | 0.26162(+02) | 0.26120(+02) |
| | CH ₄ | 0.18828(+02) | 0.18925(+02) | 0.18945(+02) | 0.18974(+02) |
| | C ₂ H ₄ | 0.33719(+02) | 0.33920(+02) | 0.33916(+02) | 0.33949(+02) |
| | CH ₃ COH | 0.57865(+02) | 0.58119(+02) | 0.58096(+02) | 0.58116(+02) |
| | C ₂ N ₂ | 0.67931(+02) | 0.68423(+02) | 0.68266(+02) | 0.68216(+02) |
| | CF ₄ | 0.13271(+03) | 0.13298(+03) | 0.13296(+03) | 0.13296(+03) |
| $n = 2$ | He | 0.57223(+01) | 0.57862(+01) | 0.58012(+01) | 0.5796(+01) ^a |
| | Ne | 0.25706(+03) | 0.25762(+03) | 0.25761(+03) | 0.25815(+03) ^a |
| | HF | 0.20005(+03) | 0.20072(+03) | 0.20069(+03) | 0.20064(+03) |
| | F ₂ | 0.40214(+03) | 0.40210(+03) | 0.40104(+03) | 0.39847(+02) |
| | H ₂ O | 0.15201(+03) | 0.15269(+03) | 0.15269(+03) | 0.15260(+03) |
| | CH ₄ | 0.80254(+02) | 0.80670(+02) | 0.80701(+02) | 0.80793(+02) |
| | C ₂ H ₄ | 0.15578(+03) | 0.15661(+03) | 0.15653(+03) | 0.15665(+03) |
| | CH ₃ COH | 0.30547(+03) | 0.30692(+03) | 0.30661(+03) | 0.30682(+03) |
| | C ₂ N ₂ | 0.36862(+03) | 0.37086(+03) | 0.37008(+03) | 0.36996(+03) |
| | CF ₄ | 0.87078(+03) | 0.87370(+03) | 0.87291(+03) | 0.87358(+03) |
| $n = 3$ | He | 0.17929(+02) | 0.18255(+02) | 0.18341(+02) | |
| | Ne | 0.35807(+04) | 0.35872(+04) | 0.35865(+04) | |
| | HF | 0.25440(+04) | 0.25499(+04) | 0.25496(+04) | 0.25541(+04) |
| | F ₂ | 0.51064(+04) | 0.51057(+04) | 0.50961(+04) | 0.51146(+04) |
| | H ₂ O | 0.17378(+04) | 0.17424(+04) | 0.17421(+04) | 0.17454(+04) |

Table 1 continued

| | HF | MP2 | CISD | Ref. [24] | |
|---------|-------------------------------|--------------|--------------|--------------|--------------|
| $n = 4$ | CH ₄ | 0.68904(+03) | 0.69074(+03) | 0.69073(+03) | 0.69290(+03) |
| | C ₂ H ₄ | 0.13723(+04) | 0.13758(+04) | 0.13752(+04) | 0.13791(+04) |
| | CH ₃ COH | 0.31077(+04) | 0.31160(+04) | 0.31136(+04) | 0.31225(+04) |
| | C ₂ N ₂ | 0.36267(+04) | 0.36368(+04) | 0.36332(+04) | 0.36413(+04) |
| | CF ₄ | 0.10847(+05) | 0.10873(+05) | 0.10864(+05) | 0.10894(+05) |
| | He | 0.98702(+02) | 0.10087(+03) | 0.10149(+03) | |
| | Ne | 0.95642(+05) | 0.95755(+05) | 0.95739(+05) | |
| | HF | 0.61702(+05) | 0.61783(+05) | 0.61786(+05) | 0.63339(+05) |
| | F ₂ | 0.12353(+06) | 0.12353(+06) | 0.12338(+06) | 0.12701(+05) |
| | H ₂ O | 0.37776(+05) | 0.37824(+05) | 0.37819(+05) | 0.38802(+05) |
| | CH ₄ | 0.11333(+05) | 0.11342(+05) | 0.11342(+05) | 0.11666(+05) |
| | C ₂ H ₄ | 0.22686(+05) | 0.22705(+05) | 0.22700(+05) | 0.23344(+05) |
| | CH ₃ COH | 0.60491(+05) | 0.60565(+05) | 0.60540(+05) | 0.62194(+05) |
| | C ₂ N ₂ | 0.66178(+05) | 0.66238(+05) | 0.66218(+05) | 0.68028(+05) |
| | CF ₄ | 0.25805(+06) | 0.25842(+06) | 0.25828(+06) | 0.26506(+06) |

^a He and Ne atoms from Ref. [16]

Table 2 (p^n) Moment values using DFT methods

| | BLYP | BVWN | SLYP | SVWN | |
|----------|-------------------------------|--------------|--------------|--------------|--------------|
| $n = -2$ | He | 0.41973(+01) | 0.41147(+01) | 0.43575(+01) | 0.42732(+01) |
| | Ne | 0.54489(+01) | 0.54245(+01) | 0.55003(+01) | 0.54761(+01) |
| | HF | 0.76255(+01) | 0.75994(+01) | 0.76932(+01) | 0.76686(+01) |
| | F ₂ | 0.11458(+02) | 0.11438(+02) | 0.11574(+02) | 0.11556(+02) |
| | H ₂ O | 0.10751(+02) | 0.10668(+02) | 0.10849(+02) | 0.10770(+02) |
| | CH ₄ | 0.18178(+02) | 0.17840(+02) | 0.18388(+02) | 0.18062(+02) |
| | C ₂ H ₄ | 0.25367(+02) | 0.24859(+02) | 0.25705(+02) | 0.25190(+02) |
| | CH ₃ COH | 0.32406(+02) | 0.31604(+02) | 0.32923(+02) | 0.32096(+02) |
| | C ₂ N ₂ | 0.29676(+02) | 0.29181(+02) | 0.30201(+02) | 0.29663(+02) |
| | CF ₄ | 0.27911(+02) | 0.27774(+02) | 0.28191(+02) | 0.28055(+02) |
| $n = -1$ | He | 0.21731(+01) | 0.21516(+01) | 0.22188(+01) | 0.21970(+01) |
| | Ne | 0.54661(+01) | 0.54523(+01) | 0.54909(+01) | 0.54772(+01) |
| | HF | 0.64589(+01) | 0.64370(+01) | 0.64909(+01) | 0.64691(+01) |
| | F ₂ | 0.10284(+02) | 0.10256(+02) | 0.10333(+02) | 0.10305(+02) |
| | H ₂ O | 0.75690(+01) | 0.75361(+01) | 0.76119(+01) | 0.75792(+01) |
| | CH ₄ | 0.10139(+02) | 0.10069(+02) | 0.10235(+02) | 0.10165(+02) |
| | C ₂ H ₄ | 0.15019(+02) | 0.14929(+02) | 0.15132(+02) | 0.15042(+02) |
| | CH ₃ COH | 0.19942(+02) | 0.19826(+02) | 0.20094(+02) | 0.19978(+02) |
| | C ₂ N ₂ | 0.20055(+02) | 0.19963(+02) | 0.20166(+02) | 0.20073(+02) |
| | CF ₄ | 0.25445(+02) | 0.25354(+02) | 0.25597(+02) | 0.25505(+02) |
| $n = 1$ | He | 0.27821(+01) | 0.28046(+01) | 0.27160(+01) | 0.27383(+01) |
| | Ne | 0.35162(+02) | 0.35207(+02) | 0.35033(+02) | 0.35078(+02) |
| | HF | 0.30395(+02) | 0.30440(+02) | 0.30267(+02) | 0.30312(+02) |
| | F ₂ | 0.59541(+02) | 0.59616(+02) | 0.59292(+02) | 0.59367(+02) |
| | H ₂ O | 0.26078(+02) | 0.26125(+02) | 0.25948(+02) | 0.25994(+02) |

Table 2 continued

| | | BLYP | BVWN | SLYP | SVWN |
|-----------------|-------------------------------|--------------|--------------|--------------|--------------|
| <i>n</i> = 2 | CH ₄ | 0.18857(+02) | 0.18914(+02) | 0.18698(+02) | 0.18754(+02) |
| | C ₂ H ₄ | 0.33813(+02) | 0.33892(+02) | 0.33570(+02) | 0.33647(+02) |
| | CH ₃ COH | 0.57956(+02) | 0.58074(+02) | 0.57585(+02) | 0.57700(+02) |
| | C ₂ N ₂ | 0.68184(+02) | 0.68296(+02) | 0.67797(+02) | 0.67909(+02) |
| | CF ₄ | 0.13271(+03) | 0.13290(+03) | 0.13207(+03) | 0.13226(+03) |
| | He | 0.57493(+01) | 0.58212(+01) | 0.54771(+01) | 0.55478(+01) |
| | Ne | 0.25698(+03) | 0.25725(+03) | 0.25536(+03) | 0.25564(+03) |
| | HF | 0.20019(+03) | 0.20044(+03) | 0.19870(+03) | 0.19895(+03) |
| | F ₂ | 0.40116(+03) | 0.40163(+03) | 0.39809(+03) | 0.39856(+03) |
| | H ₂ O | 0.15227(+03) | 0.15249(+03) | 0.15090(+03) | 0.15112(+03) |
| | CH ₄ | 0.80457(+02) | 0.80671(+02) | 0.79255(+02) | 0.79463(+02) |
| | C ₂ H ₄ | 0.15616(+03) | 0.15651(+03) | 0.15400(+03) | 0.15434(+03) |
| | CH ₃ COH | 0.30604(+03) | 0.30659(+03) | 0.30250(+03) | 0.30306(+03) |
| | C ₂ N ₂ | 0.36952(+03) | 0.37015(+03) | 0.36524(+03) | 0.36587(+03) |
| <i>n</i> = 3 | CF ₄ | 0.87155(+03) | 0.87267(+03) | 0.86446(+03) | 0.86559(+03) |
| | He | 0.18459(+02) | 0.18702(+02) | 0.17226(+02) | 0.17460(+02) |
| | Ne | 0.35757(+04) | 0.35782(+04) | 0.35469(+04) | 0.35494(+04) |
| | HF | 0.25413(+04) | 0.25436(+04) | 0.25166(+04) | 0.25189(+04) |
| | F ₂ | 0.50893(+04) | 0.50940(+04) | 0.50376(+04) | 0.50423(+04) |
| | H ₂ O | 0.17370(+04) | 0.17390(+04) | 0.17160(+04) | 0.17180(+04) |
| | CH ₄ | 0.68989(+03) | 0.69149(+03) | 0.67581(+03) | 0.67738(+03) |
| | C ₂ H ₄ | 0.13730(+04) | 0.13759(+04) | 0.13462(+04) | 0.13491(+04) |
| | CH ₃ COH | 0.31066(+04) | 0.31116(+04) | 0.30591(+04) | 0.30641(+04) |
| | C ₂ N ₂ | 0.36257(+04) | 0.36321(+04) | 0.35658(+04) | 0.35721(+04) |
| <i>n</i> = 4 | CF ₄ | 0.10836(+05) | 0.10847(+05) | 0.10725(+05) | 0.10735(+05) |
| | He | 0.10415(+03) | 0.10538(+03) | 0.95906(+02) | 0.97075(+02) |
| | Ne | 0.95365(+05) | 0.95418(+05) | 0.94492(+05) | 0.94545(+05) |
| | HF | 0.61524(+05) | 0.61572(+05) | 0.60831(+05) | 0.60879(+05) |
| | F ₂ | 0.12301(+06) | 0.12311(+06) | 0.12155(+06) | 0.12166(+06) |
| | H ₂ O | 0.37685(+05) | 0.37726(+05) | 0.37148(+05) | 0.37189(+05) |
| | CH ₄ | 0.11341(+05) | 0.11369(+05) | 0.11058(+05) | 0.11086(+05) |
| | C ₂ H ₄ | 0.22680(+05) | 0.22734(+05) | 0.22137(+05) | 0.22191(+05) |
| | CH ₃ COH | 0.60369(+05) | 0.60466(+05) | 0.59296(+05) | 0.59393(+05) |
| | C ₂ N ₂ | 0.66075(+05) | 0.66200(+05) | 0.64740(+05) | 0.64866(+05) |
| CF ₄ | 0.25730(+06) | 0.25753(+06) | 0.25427(+06) | 0.25450(+06) | |

show higher differences than the post-HF densities. In the study of the dependence of $p^2\Delta\gamma(p)$, CISD and BLYP, with the intermolecular distance of two diatomic molecules, we find that CISD density is more sensitive to this variable than BLYP.

Finally, we have computed the power of p for several molecular systems obtaining conclusions which are similar to those recently presented in Ref. [24].

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