

A postulate involving quantum mechanical momentum in position space, density function expression of the kinetic energy and Heisenberg's uncertainty relation

Ramon Carbó-Dorca · Emili Besalú

Received: 2 June 2013 / Accepted: 15 April 2014 / Published online: 25 May 2014
© Springer International Publishing Switzerland 2014

Abstract A postulate is enunciated involving the construction of the quantum mechanical linear momentum vector in position space. This proposal leads to a coherent Heisenberg uncertainty relation for a Gaussian model density function. Such result is then used as starting point to obtain algorithms to perform kinetic energy calculations, when only the density function of a given system is known. The general theoretical framework is described and several density function types, including ab initio formulation, are used as application examples.

Keywords Momentum operator in position space · Gaussian model density functions · Heisenberg's uncertainty · Kinetic energy · Atomic shell approximation density functions · LCAO MO density functions

1 Introduction

The nature of the kinetic energy in quantum mechanics constitutes an old problem which has been deeply studied since the need of an operator description in quantum mechanics up to recent times, see for example [1–3] and references therein. In order to spare a large set of references, the authors encourage the potential readers to use the ones provided by the previous citations. The first quotation [1] clearly identifies the ambiguous nature of kinetic energy and provides a helpful set of hints which can be considered to obtain alternative expressions for it. One can say the present contribution relies essentially on such starting point, while trying to find out another kind of plausible path towards kinetic energy practical evaluation.

R. Carbó-Dorca (✉) · E. Besalú
Institut de Química Computacional i Catàlisi (IQCC), Universitat de Girona, 17071
Catalonia, Girona, Spain
e-mail: quantumqsar@hotmail.com

The present work cannot be seen as an isolated contribution to the solving of the quantum mechanical kinetic energy nature problem. It must be considered as the first step to set up a computational system allowing quantum chemically based studies of very large molecules under approximate density function knowledge, like the one provided by the atomic shell approximation [10–12].

Furthermore, if this contribution has to be fully justified, one can state the fact consisting into that a computational problem appears when, for some practical reason, there is needed the kinetic energy value of some system and only the first order density function is known. This could be the case in DFT procedures like the well-known and widespread Kohn-Sham method [4]. The present paper tries to develop a possible approximate but reasonable solution to this enunciate.

The basic approach suggested here proposes a *postulate*. Such working scheme possibility considers the momentum vector representation in position space might be directly constructed from the usual gradient-like, quantum mechanical momentum operator. As an initial step, it will be shown that such a postulate provides a coherent Heisenberg's indetermination picture for a system, solely defined by means of a schematic density function. Such a result could indicate the postulated description of momentum in position space can be admitted as a reasonable workout proposal demanding further development. Also the coherent connection of the proposed kinetic energy evaluation problem with Heisenberg's uncertainty relations will be also discussed as a hint of the reasonable computational framework, which can be easily developed afterwards.

The scheme of this contribution can be therefore described as follows. First an analysis involving a model system made by a Gaussian function is discussed. To this introduction it will follow a general point of view of the problem, which opens the way to study three related application examples. Another simple density function made by two Gaussian functions centered at two different points of space will be studied in a first place. A simplified density function under the ASA scheme will be developed as a second example. A third example related to the simplified form of nuclear density functions will be described in full. Finally, the use of ab initio density functions to obtain momentum variances and the kinetic energy will end the present study.

2 Postulating momentum representation in position space and the connection with Heisenberg indetermination relation in a Gaussian density function framework

One can start proposing to use a unique Gaussian function as a model density function, which can be defined like:

$$\gamma(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} g(\mathbf{r}|\alpha) = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \exp(-\alpha|\mathbf{r}|^2) \rightarrow \langle\gamma(\mathbf{r})\rangle = 1.$$

It is irrelevant that the Gaussian center can be located in another point of space, say $\mathbf{R} \neq \mathbf{0}$, or not.

In this simple example the mean position will be zero, and one can write accordingly:

$$\langle \mathbf{r} \rangle \equiv \langle \mathbf{r} \gamma(\mathbf{r}) \rangle = \mathbf{0}.$$

The position variance can be also easily written in three dimensional spaces, as the following integral can be proposed to evaluate it:

$$\text{var}(\mathbf{r}) = \left\langle |\mathbf{r}|^2 \gamma(\mathbf{r}) \right\rangle = \frac{3}{2\alpha}.$$

On the other hand, as it is well-known in time independent quantum mechanics, the momentum operator can be written as the gradient operator: $i\hbar \frac{\partial}{\partial \mathbf{r}}$ and thus its effect on the Gaussian density function model can be also readily obtained as:

$$\mathbf{p} \equiv i\hbar \frac{\partial}{\partial \mathbf{r}} \gamma(\mathbf{r}) = -2\alpha i\hbar \mathbf{r} \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \exp(-\alpha |\mathbf{r}|^2) = -2\alpha i\hbar \mathbf{r} \gamma(\mathbf{r})$$

Taking as a *postulate* the equivalence in the upper expression and considering the result consequently as a momentum representation in position space, one can also see that the mean momentum will be null, admitting as a part of the postulate, that it can be also written:

$$\langle \mathbf{p} \rangle \equiv -2\alpha i\hbar \langle \mathbf{r} \gamma(\mathbf{r}) \rangle = \mathbf{0}$$

Then according to the momentum representation postulate, the squared module of the momentum expression can be also considered as a Euclidean norm:

$$|\mathbf{p}|^2 = \mathbf{p}^* \cdot \mathbf{p} \equiv 4\alpha^2 \hbar^2 |\mathbf{r} \gamma(\mathbf{r})|^2,$$

so the momentum variance can be readily computed as:

$$\langle |\mathbf{p}|^2 \rangle \equiv \text{var}(\mathbf{p}) \equiv 4\alpha^2 \hbar^2 \left(\frac{\alpha}{\pi}\right)^3 \int_D |\mathbf{r}|^2 \exp(-2\alpha |\mathbf{r}|^2) dV = 3\alpha \left(\frac{\alpha}{2\pi}\right)^{\frac{3}{2}} \hbar^2$$

It must be noted and stressed here that the momentum squared module is not obtained like in the usual quantum mechanical way, but taking into account the imaginary numbers algebra. So, using instead of $i^2 = -1$, the positive real result issuing from: $|i|^2 = i^*i = (-i)i = +1$.

2.1 Heisenberg indetermination

Thus, the product of both position and momentum variances might be written as:

$$\text{var}(\mathbf{r}) \text{var}(\mathbf{p}) \equiv \left[\frac{3}{2\alpha} \right] \left[3\alpha \left(\frac{\alpha}{2\pi}\right)^{\frac{3}{2}} \hbar^2 \right] = \frac{9}{2} \left(\frac{\alpha}{2\pi}\right)^{\frac{3}{2}} \hbar^2,$$

the factor 9 is obviously related to the dimension of position space. This result can be also interpreted as constituting a statement of Heisenberg indetermination relation, attached to this simple Gaussian model density and the postulated momentum representation in position space. It can be expressed in an equivalent way, just taking the square root of both sides, thus resulting into an alternative Heisenberg's relation, but now involving the position and momentum standard deviations:

$$\sigma(\mathbf{r}) \sigma(\mathbf{p}) \equiv \frac{3\sqrt{2}}{2} \left(\frac{\alpha}{2\pi} \right)^{\frac{3}{4}} \hbar.$$

The appearance of the Gaussian exponent might indicate the connection with the nature of the density described object, *sharper* (more localized) this object becomes the factor will increase, *softer* (more delocalized) the object density appears, and then the factor will diminish. At the extreme values the point-like and completely widespread object charges respectively, the factor becomes infinite and zero, corresponding to what can be considered completely localized and delocalized descriptions.

It must be noted the fact that both position and momentum variances possess the Gaussian exponent in inverse and direct proportion respectively. So, sharper the density, then momentum variance will grow, while the position variance will decrease and such situation will appear reversed when softer the density distribution becomes.

Such a result must be compared with a previous published one, where the momentum representation in momentum space was employed [5] to obtain a Heisenberg indetermination formula. In this previous case the presence of the Gaussian exponent was not present at the right of the equality.

3 Momentum representation postulate and Heisenberg indetermination relation in a general density expression

Given a density function: $\rho(\mathbf{r})$, attached to any submicroscopic system, such coherent result between the postulated momentum definition in position space and the indetermination principle obtained in the previously studied Gaussian model, precludes the possibility to extend as a *general postulate* the following definition of momentum in position space:

$$\mathbf{p} \equiv i\hbar \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}).$$

In this case the mean position and momentum values can be non-null and their squared modules will be needed in the corresponding variance definitions, like:

$$\langle \mathbf{r} \rangle \equiv \langle \mathbf{r} \rho(\mathbf{r}) \rangle \rightarrow |\langle \mathbf{r} \rangle|^2 \equiv |\langle \mathbf{r} \rho(\mathbf{r}) \rangle|^2,$$

an expression which is related to the dipole momentum expectation value. Thus, in atoms and apolar molecular structures such value is null, like in the previous Gaussian model case. The postulated momentum will furnish the following expectation value:

$$\langle \mathbf{p} \rangle \equiv \left\langle i\hbar \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) \right\rangle \rightarrow |\langle \mathbf{p} \rangle|^2 \equiv \hbar^2 \left\langle \left| \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) \right|^2 \right\rangle$$

and the corresponding variances could be written accordingly. First, one can write:

$$\text{var}(\mathbf{r}) \equiv \langle |\mathbf{r}|^2 \rho(\mathbf{r}) \rangle - |\langle \mathbf{r} \rho(\mathbf{r}) \rangle|^2,$$

which can be related to the trace of the quadrupole momentum tensor as well as to the squared module of the dipole moment, and thus it is resulting into a definite non-negative parameter, translationally and rotationally invariant. Then, the postulated momentum variance will be computed as:

$$\text{var}(\mathbf{p}) \equiv \hbar^2 \left\langle \left| \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) \right|^2 \right\rangle - \hbar^2 \left\langle \left| \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) \right| \right\rangle^2.$$

Both variances can be furthermore used to write its product as it has been done before:

$$\text{var}(\mathbf{r}) \text{var}(\mathbf{p}) \equiv \hbar^2 \text{var}(\mathbf{r}) \text{var} \left(\frac{\partial}{\partial \mathbf{r}} \right) = \lambda^2 \hbar^2,$$

a final expression which can be easily reduced to the standard deviations:

$$\sigma(\mathbf{r}) \sigma(\mathbf{p}) \equiv \lambda \hbar.$$

These last results constitute a general form of Heisenberg's indetermination relationships, defined within the proposed postulate about the nature of momentum in position space.

3.1 Kinetic energy

The way the electronic kinetic energy K can be defined in these circumstances becomes quite an easy task. Using the usual expression in terms of the squared momentum, it can be obtained:

$$K \equiv \frac{1}{2m} |\mathbf{p}|^2 \equiv \frac{\hbar^2}{2m} \left\langle \left| \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) \right|^2 \right\rangle,$$

which can be considered for practical purposes as a computational rule, derived from the postulated form of the linear momentum. The above result constituting a suitable evaluation of the kinetic energy in some common general way, which can be employed in cases where only the density function of some system it is known and available, as commented at the introduction.

For instance, in the one Gaussian density function model example, earlier developed one can write:

$$K \equiv \frac{3\alpha}{2m} \left(\frac{\alpha}{2\pi} \right)^{\frac{3}{2}} \hbar^2.$$

4 Diatomic molecule model

Having developed the initial working scheme in an atomic-like model example and having described the general procedure for evaluating kinetic energy using solely the density function knowledge, it is time to provide several practical illustrations, starting again with a simple diatomic scheme and extending it afterwards to more involved complex density function environments.

Suppose, thus, as starting model, some simplified density function expression associated to a diatomic molecule. This density function can be chosen as a superposition of two Gaussian functions, centered at two points in space $\{\mathbf{R}_A; \mathbf{R}_B\}$, assuming to the pair of coefficients set $\{Q_A; Q_B\}$ might correspond to some atomic population choice, their sum being the total number of electrons N_e :

$$\rho(\mathbf{r}) = Q_A \gamma(\mathbf{r} - \mathbf{R}_A | \alpha) + Q_B \gamma(\mathbf{r} - \mathbf{R}_B | \beta) \leftarrow Q_A + Q_B = N_e.$$

The postulated momentum in the way proposed in this paper can be written now as:

$$\mathbf{p} \equiv i\hbar \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) = -2i\hbar \left(\alpha Q_A (\mathbf{r} - \mathbf{R}_A) \gamma(\mathbf{r} - \mathbf{R}_A | \alpha) + \beta Q_B (\mathbf{r} - \mathbf{R}_B) \gamma(\mathbf{r} - \mathbf{R}_B | \beta) \right)$$

and the corresponding momentum squared module can be now computed as:

$$|\mathbf{p}|^2 \equiv 4\hbar^2 \left[\begin{aligned} &(\alpha Q_A)^2 |\mathbf{r} - \mathbf{R}_A|^2 \left(\frac{\alpha}{\pi} \right)^3 \exp(-2\alpha |\mathbf{r} - \mathbf{R}_A|^2) \\ &+ (\beta Q_B)^2 |\mathbf{r} - \mathbf{R}_B|^2 \left(\frac{\beta}{\pi} \right)^3 \exp(-2\beta |\mathbf{r} - \mathbf{R}_B|^2) \\ &+ (\alpha\beta Q_A Q_B (\mathbf{r} - \mathbf{R}_A) \cdot (\mathbf{r} - \mathbf{R}_B) \gamma(\mathbf{r} - \mathbf{R}_A | \alpha) \gamma(\mathbf{r} - \mathbf{R}_B | \beta)) \end{aligned} \right]$$

Defining: $\sigma = \alpha + \beta$, then the two Gaussian product of the last term can transform into the usual form of a new Gaussian, centered at the point: $\mathbf{P} = \sigma^{-1} (\alpha \mathbf{R}_A + \beta \mathbf{R}_B)$ with exponent σ and multiplied by a factor: $\kappa = \exp\left(-\frac{\alpha\beta}{\sigma} |\mathbf{R}_A - \mathbf{R}_B|^2\right)$. That is, one can easily write (see for example: [6]):

$$\gamma(\mathbf{r} - \mathbf{R}_A | \alpha) \gamma(\mathbf{r} - \mathbf{R}_B | \beta) = \kappa \left(\frac{\alpha\beta}{\pi^2} \right)^{\frac{3}{2}} g(\mathbf{r} - \mathbf{P} | \sigma).$$

Thus, integration of the above squared momentum expression will produce:

$$\langle |\mathbf{p}|^2 \rangle \equiv 4\hbar^2 \left[\begin{aligned} &(\alpha Q_A)^2 \left(\frac{\alpha}{\pi} \right)^3 \langle |\mathbf{r}|^2 \exp(-2\alpha |\mathbf{r}|^2) \rangle \\ &+ (\beta Q_B)^2 \left(\frac{\beta}{\pi} \right)^3 \langle |\mathbf{r}|^2 \exp(-2\beta |\mathbf{r}|^2) \rangle \\ &+ \alpha\beta \left(\frac{\alpha\beta}{\pi^2} \right)^{\frac{3}{2}} \kappa Q_A Q_B \langle (\mathbf{r} - \mathbf{R}_A) \cdot (\mathbf{r} - \mathbf{R}_B) g(\mathbf{r} - \mathbf{P} | \sigma) \rangle \end{aligned} \right]$$

or what is the same:

$$\langle |\mathbf{p}|^2 \rangle \equiv 4\hbar^2 \left[\frac{3}{4} \left(\alpha \left(\frac{\alpha}{2\pi} \right)^{\frac{3}{2}} Q_A^2 + \beta \left(\frac{\beta}{2\pi} \right)^{\frac{3}{2}} Q_B^2 \right) + \alpha\beta \left(\frac{\alpha\beta}{\pi^2} \right)^{\frac{3}{2}} \kappa Q_A Q_B \langle (\mathbf{r} - \mathbf{R}_A) \cdot (\mathbf{r} - \mathbf{R}_B) g(\mathbf{r} - \mathbf{P} | \sigma) \rangle \right]$$

There follows the integral still to be evaluated, which can be written as:

$$\langle (\mathbf{r} - \mathbf{R}_A) \cdot (\mathbf{r} - \mathbf{R}_B) g(\mathbf{r} - \mathbf{P} | \sigma) \rangle = \left(\frac{3}{2\sigma} + P_{AB} \right) \left(\frac{\pi}{\sigma} \right)^{\frac{3}{2}}$$

So, the final form of the integral needed for the momentum variance evaluation can be written in this case as:

$$\langle |\mathbf{p}|^2 \rangle \equiv 4\hbar^2 \left[\frac{3}{4} \left(\alpha \left(\frac{\alpha}{2\pi} \right)^{\frac{3}{2}} Q_A^2 + \beta \left(\frac{\beta}{2\pi} \right)^{\frac{3}{2}} Q_B^2 \right) + \alpha\beta \left(\frac{\alpha\beta}{\pi^2} \right)^{\frac{3}{2}} \left(\frac{3}{2\sigma} + P_{AB} \right) \kappa Q_A Q_B \right]$$

with the additional definition:

$$P_{AB} = -\alpha\beta\sigma^{-2} |\mathbf{R}_A - \mathbf{R}_B|^2$$

then, the integral of the momentum squared module becomes:

$$\langle |\mathbf{p}|^2 \rangle \equiv 4\hbar^2 \left[\frac{3}{4} \left(\alpha \left(\frac{\alpha}{2\pi} \right)^{\frac{3}{2}} Q_A^2 + \beta \left(\frac{\beta}{2\pi} \right)^{\frac{3}{2}} Q_B^2 \right) + \frac{\alpha\beta}{\sigma} \left(\frac{\alpha\beta}{\pi^2} \right)^{\frac{3}{2}} \left(\frac{3}{2} - \frac{\alpha\beta}{\sigma} |\mathbf{R}_A - \mathbf{R}_B|^2 \right) \kappa Q_A Q_B \right].$$

In a first instance it must be noted that the above resultant integral for the momentum variance, under this simplified computational framework appears to be rotationally and translationally invariant, as it depends, among other irrelevant parameters, on the relevant squared distance between the two considered atomic centers.

Such a final expression constitutes also a suitable model for the cases where the density function is written as a linear combination of atomic density function parts, as it will be commented below. From the above final expression of the squared momentum the kinetic energy can be easily deduced.

4.1 Soft nuclear case

Inspired in the work of Andrae [7] and some previous discussion on finite nuclear charge density [8], a Gaussian nuclear charge density has been recently proposed and

employed in evaluating completely soft MEP surfaces [9]. Within this soft nuclear model it can be supposed that in the diatomic model discussed above, the following simplifications will hold:

$$\alpha = \beta \wedge Q_A = Z_A \wedge Q_B = Z_B \wedge \kappa = \exp\left(-\frac{\alpha}{2} |\mathbf{R}_A - \mathbf{R}_B|^2\right),$$

therefore in this case it can be also written:

$$\langle |\mathbf{p}|^2 \rangle \equiv 3\alpha \left(\frac{\alpha}{2\pi}\right)^{\frac{3}{2}} \left[Z_A^2 + Z_B^2 + \kappa \left(1 - \frac{\alpha}{3} |\mathbf{R}_A - \mathbf{R}_B|^2\right) Z_A Z_B \right] \hbar^2.$$

When both contributions are related to the same atom kind, a further simplified form can be written, as: $Z_A = Z_B = Z$; so the momentum squared module can be expressed now like:

$$\langle |\mathbf{p}|^2 \rangle \equiv 3\alpha \left(\frac{\alpha}{2\pi}\right)^{\frac{3}{2}} \left[2 + \kappa \left(1 - \frac{\alpha}{3} |\mathbf{R}_A - \mathbf{R}_B|^2\right) \right] Z^2 \hbar^2.$$

In the above integral the nuclear charge acts as a scale factor. A rough calculation indicates there is a minimal mean momentum squared module, thus also kinetic energy becomes minimal for every exponent when distance varies. Note that at zero distance it will be also obtained:

$$\langle |\mathbf{p}|^2 \rangle \equiv 9\alpha \left(\frac{\alpha}{2\pi}\right)^{\frac{3}{2}} Z^2 \hbar^2,$$

which constitutes a coherent expression in accord with the one Gaussian model density function, as discussed in first instance.

5 ASA density function model

Atomic Shell Approximation (ASA) of atomic density functions [10–12] constitute a general approximation, related to the electronic atomic density functions, which has been employed to perform customarily quantum similarity calculations, see for example: [13–18]. Because of the simple nature of ASA density functions, this scheme has been chosen here as the second application example of the postulate about momentum structure in position space and the possibility to obtain kinetic energy from density functions.

The molecular ASA density functions can be easily described as a linear combination of a set made of atomic shape ASA functions:

$$\{\sigma_I(\mathbf{r} - \mathbf{R}_I) | I = 1, N\} \rightarrow \forall I : \langle \sigma_I(\mathbf{r} - \mathbf{R}_I) \rangle = 1,$$

which in turn are generally defined as convex linear combinations of a given fixed number of s-type, Minkowski normalized, Gaussian functions. Such convex combinations have been previously fitted to the ab initio density functions of

atomic structures, constructing in this way some optimally chosen GTO basis set: $\{\forall I : \gamma(\mathbf{r} - \mathbf{R}_I | \alpha_\mu^I) | \mu = 1, n_I\}$.

Therefore the ASA optimized atomic shape functions can be written like:

$$\forall I : \sigma_I(\mathbf{r} - \mathbf{R}_I) = \sum_{\mu=1}^{n_I} c_\mu^I \gamma(\mathbf{r} - \mathbf{R}_I | \alpha_\mu^I) \rightarrow \langle \sigma_I \rangle = \sum_{\mu=1}^{n_I} c_\mu^I \langle \gamma_\mu^I \rangle = \sum_{\mu=1}^{n_I} c_\mu^I = 1.$$

In constructing approximate molecular density functions, each ASA shape function defined as above is supposedly centered at the N atomic sites $\{\mathbf{R}_I | I = 1, N\}$ of a given molecular structure. The molecular density function is thus constructed as a linear combination of atomic centered ASA shape functions, employing as coefficients a given set of atomic populations $\{Q_I | I = 1, N\}$, which in turn contain the extra condition to sum up to the number of electrons of the attached molecule, that is: $\sum_{I=1}^N Q_I = N_e$. Therefore the molecular ASA densities can be written like:

$$\rho(\mathbf{r}) = \sum_{I=1}^N Q_I \sigma_I(\mathbf{r} - \mathbf{R}_I).$$

5.1 Postulated momentum structure

Evaluation of the postulated form of the momentum operator in position space can be written now over such ASA molecular density functions as:

$$\mathbf{p} \equiv i\hbar \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) = i\hbar \sum_{I=1}^N Q_I \frac{\partial}{\partial \mathbf{r}} \sigma_I(\mathbf{r} - \mathbf{R}_I) = -2i\hbar \sum_{I=1}^N Q_I (\mathbf{r} - \mathbf{R}_I) \theta_I(\mathbf{r} - \mathbf{R}_I)$$

where the new function set $\{\theta_I(\mathbf{r} - \mathbf{R}_I) | I = 1, N\}$ is easily defined by:

$$\forall I : \theta_I(\mathbf{r} - \mathbf{R}_I) = \sum_{\mu=1}^{n_I} c_\mu^I \alpha_\mu^I \gamma(\mathbf{r} - \mathbf{R}_I | \alpha_\mu^I).$$

The expectation value of the momentum can be evaluated in the way previously done, so there are the following integrals to be evaluated for this purpose:

$$\forall I, \mu : \langle (\mathbf{r} - \mathbf{R}_I) \gamma(\mathbf{r} - \mathbf{R}_I | \alpha_\mu^I) \rangle \rightarrow \left\{ \left\langle (x_K - X_{K,I}) \gamma(\mathbf{r} - \mathbf{R}_I | \alpha_\mu^I) \right\rangle | K = 1, 3 \right\};$$

but this kind of integrals are null, as it has been found beforehand. Thus, the variance of momentum will correspond only to the integral about its squared module:

$$\langle |\mathbf{p}|^2 \rangle \equiv 4\hbar^2 \sum_{I=1}^N \sum_{J=1}^N Q_I Q_J \langle [(\mathbf{r} - \mathbf{R}_I) \cdot (\mathbf{r} - \mathbf{R}_J)] \theta_I(\mathbf{r} - \mathbf{R}_I) \theta_J(\mathbf{r} - \mathbf{R}_J) \rangle,$$

which reduces the problem to the evaluation of integrals like:

$$\forall I, J; \mu, \lambda : Z_{\mu\lambda}^{IJ} = \alpha_{\mu}^I \alpha_{\lambda}^J \left\langle [(\mathbf{r} - \mathbf{R}_I) \cdot (\mathbf{r} - \mathbf{R}_J)] \gamma(\mathbf{r} - \mathbf{R}_I | \alpha_{\mu}^I) \gamma(\mathbf{r} - \mathbf{R}_J | \alpha_{\lambda}^J) \right\rangle,$$

which in turn are related with the aforementioned two center momentum variance integrals, previously studied within the two Gaussian functions diatomic density function model.

Indeed, calling now: $\sigma = \alpha_{\mu}^I + \alpha_{\lambda}^J$, the two Gaussian product can transform, as it has been used beforehand, into the usual form of a new Gaussian, centered at the point: $\mathbf{P} = \sigma^{-1} (\alpha_{\mu}^I \mathbf{R}_I + \alpha_{\lambda}^J \mathbf{R}_J)$ with exponent σ and multiplied by a factor:

$$\kappa = \exp\left(-\frac{\alpha_{\mu}^I \alpha_{\lambda}^J}{\sigma} |\mathbf{R}_I - \mathbf{R}_J|^2\right). \text{ Then, the relevant integral becomes:}$$

$$Z_{\mu\lambda}^{IJ} = \alpha_{\mu}^I \alpha_{\lambda}^J \left(\frac{\alpha_{\mu}^I \alpha_{\lambda}^J}{\pi^2}\right)^{\frac{3}{2}} \kappa \langle [(\mathbf{r} - \mathbf{P} + \mathbf{P} - \mathbf{R}_I) \cdot (\mathbf{r} - \mathbf{P} + \mathbf{P} - \mathbf{R}_J)] g(\mathbf{r} - \mathbf{P} | \sigma) \rangle,$$

and as it was also used before, one can consider the following equality:

$$(\mathbf{P} - \mathbf{R}_I) \cdot (\mathbf{P} - \mathbf{R}_J) = -\alpha_{\mu}^I \alpha_{\lambda}^J \sigma^{-2} |\mathbf{R}_I - \mathbf{R}_J|^2.$$

Thus, the general integral to be employed within the ASA framework in order to evaluate the ASA kinetic energy can be finally written as a result, which it is also totally coincident with the formerly described diatomic integral:

$$Z_{\mu\lambda}^{IJ} = \frac{\alpha_{\mu}^I \alpha_{\lambda}^J}{\sigma} \left(\frac{\alpha_{\mu}^I \alpha_{\lambda}^J}{\pi \sigma}\right)^{\frac{3}{2}} \kappa \left(\frac{3}{2} - \frac{\alpha_{\mu}^I \alpha_{\lambda}^J}{\sigma} |\mathbf{R}_I - \mathbf{R}_J|^2\right).$$

6 Kinetic energy in soft nuclear Gaussian density functions (SNGDF)

This section enlarges the previous Sect. 4.1, including a general study of nuclear DF. The nature of SNGDF has been recently discussed in terms of molecular electrostatic potentials, see for example reference [9], and proposed in a more general context to substitute the usual point-like nuclear repulsion [19]. Although the form of SNGDF resembles the previously employed ASA molecular DF it is essentially different as it will be shown below. However, this apparent simplicity allows to use it as an application example of the way kinetic energy from DF knowledge can be obtained. This feature has been the reason why it is included in the present work.

The simplest way a SNGDF can be written can be proposed as follows:

$$\rho(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \sum_I Z_I \exp\left(-\alpha |\mathbf{r} - \mathbf{R}_I|^2\right)$$

where the sum runs over all the nuclei; for the I -th nucleus located at the position \mathbf{R}_I , then Z_I is the corresponding atomic number, while a parameter α , associated to the sharpness of the density peaks centered at each nucleus, is considered homogeneous for every nuclear charge density. The scale factor appearing in front is nothing else than the common Minkowski norm of the Gaussian functions appearing within the sum.

According to the postulate on kinetic energy described in the present work and which has been earlier described, the momentum generated by such a DF, can be calculated easily as the nuclear density scaled gradient:

$$\mathbf{p} = i\hbar \frac{\partial \rho}{\partial \mathbf{r}} = -2i\hbar\alpha \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \sum_I \left[Z_I \exp\left(-\alpha |\mathbf{r} - \mathbf{R}_I|^2\right) (\mathbf{r} - \mathbf{R}_I) \right],$$

And moreover defining the vector expression:

$$\omega = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \sum_I \left[Z_I \exp\left(-\alpha |\mathbf{r} - \mathbf{R}_I|^2\right) \mathbf{R}_I \right];$$

then, the momentum can be compactly written with the vector expression:

$$\mathbf{p} = -2i\hbar\alpha [\rho(\mathbf{r}) \mathbf{r} - \omega].$$

Thus, the kinetic energy could be computed by means of the sum of scalar products of functions and vectors. However, in a more realistic way than in Sect. 4.1, in order to include the nuclear masses in the global kinetic energy expression, the contributions within the summation will be scaled by the factors: $\forall I, J : \mu_{IJ} = 2 \frac{Z_I Z_J}{\sqrt{M_I M_J}}$. The factor 2 corresponds to the gradient common scale and the rest is equivalent as to use a weighted soft nuclear density, where the atomic numbers Z_I , in order to take in consideration the inhomogeneity of the nuclear masses, have been substituted by themselves divided by the square root of the corresponding nuclear mass M_I in the following way:

$$\forall I : Z_I \Rightarrow \frac{Z_I}{\sqrt{M_I}};$$

Then using the symbol:

$$E(\mathbf{R}_I; \mathbf{R}_J) = \exp\left(-\alpha |\mathbf{r} - \mathbf{R}_I|^2\right) \exp\left(-\alpha |\mathbf{r} - \mathbf{R}_J|^2\right)$$

one can write the soft nuclear kinetic energy expression as:

$$K \equiv \frac{1}{2} |\mathbf{p}|^2 = \hbar^2 \frac{\alpha^5}{\pi^3} \sum_I \sum_J \mu_{IJ} \int_D |\mathbf{r} - \mathbf{R}_I| * |\mathbf{r} - \mathbf{R}_J| E(\mathbf{R}_I; \mathbf{R}_J) d\mathbf{r},$$

which can be expressed in turn as the sum of the three integrals:

$$I_0 = \frac{\alpha^5}{\pi^3} \sum_I \sum_J \mu_{IJ} (\mathbf{R}_I * \mathbf{R}_J) \int_D E(\mathbf{R}_I; \mathbf{R}_J) d\mathbf{r},$$

$$I_1 = -\frac{\alpha^5}{\pi^3} \sum_I \sum_J \mu_{IJ} (\mathbf{R}_I + \mathbf{R}_J) * \int_D \mathbf{r} E(\mathbf{R}_I; \mathbf{R}_J) d\mathbf{r}$$

and:

$$I_2 = \frac{\alpha^5}{\pi^3} \sum_I \sum_J \mu_{IJ} \int_D |\mathbf{r}|^2 E(\mathbf{R}_I; \mathbf{R}_J) d\mathbf{r}$$

The basic integral involved in I_0 is simply an overlap integral between two normalized s-type GTO, so one can write:

$$S_{IJ} = \left(\frac{\alpha}{\pi}\right)^3 \int_D E(\mathbf{R}_I; \mathbf{R}_J) d\mathbf{r}$$

The integral appearing in I_1 can be expressed as a dipole moment auxiliary integral between two 1s normalized GTO, in the way:

$$\mathbf{M}_{IJ} = \left(\frac{\alpha}{\pi}\right)^3 \int_D \mathbf{r} E(\mathbf{R}_I; \mathbf{R}_J) d\mathbf{r}.$$

Finally, I_2 can be written in compact form by means of the integral:

$$Q_{IJ} = \left(\frac{\alpha}{\pi}\right)^3 \int_D |\mathbf{r}|^2 E(\mathbf{R}_I; \mathbf{R}_J) d\mathbf{r},$$

which coincides with the trace of the quadrupole moment integrals, involving in this way the sum of three integrals like:

$$X_{IJ} = \left(\frac{\alpha}{\pi}\right)^3 \int_D x^2 E(\mathbf{R}_I; \mathbf{R}_J) d\mathbf{r},$$

in this manner, substituting x one at a time by y and z , one can write:

$$Q_{IJ} = X_{IJ} + Y_{IJ} + Z_{IJ}.$$

The form of the nuclear kinetic energy will depend on the usual product of two GTO in general centered at two space sites. Taking into account that the central point $\mathbf{R}_P = \frac{1}{2}(\mathbf{R}_I + \mathbf{R}_J)$ has to be previously defined, then it is well-known that it can be written:

$$E(\mathbf{R}_I; \mathbf{R}_J) = \exp\left(-\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_J|^2\right) \exp\left(-2\alpha |\mathbf{r} - \mathbf{R}_P|^2\right)$$

Therefore, the involved integrals can be rewritten as follows. First the overlap will produce:

$$\begin{aligned} S_{IJ} &= \left(\frac{\alpha}{\pi}\right)^3 \exp\left(-\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_J|^2\right) \int_D \exp\left(-2\alpha |\mathbf{r} - \mathbf{R}_P|^2\right) d\mathbf{r} \\ &= \left(\frac{\alpha}{\pi}\right)^3 \exp\left(-\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_J|^2\right) \left(\frac{\pi}{2\alpha}\right)^{\frac{3}{2}} = \left(\frac{\alpha}{2\pi}\right)^{\frac{3}{2}} \exp\left(-\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_J|^2\right) \end{aligned}$$

Second, writing the dipole moment integrals after the manipulation of the GTO product, provides:

$$\mathbf{M}_{IJ} = \left(\frac{\alpha}{\pi}\right)^3 \exp\left(-\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_J|^2\right) \int_D \mathbf{r} \exp\left(-2\alpha |\mathbf{r} - \mathbf{R}_P|^2\right) d\mathbf{r}$$

which will depend on the integral kind:

$$\delta_x = \int_{-\infty}^{+\infty} x e^{-2\alpha(x-X_P)^2} dx = X_P \left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}};$$

So, the dipole vector can be written as the overlap scaled midpoint of both GTO centers:

$$\mathbf{M}_{IJ} = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \exp\left(-\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_J|^2\right) \mathbf{R}_P = S_{IJ} \mathbf{R}_P = \frac{1}{2} S_{IJ} (\mathbf{R}_I + \mathbf{R}_J).$$

Finally, the intervening quadrupole integrals can be obtained as:

$$X_{IJ} = \left(\frac{\alpha}{\pi}\right)^3 \exp\left(-\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_J|^2\right) \int_D x^2 \exp\left(-2\alpha |\mathbf{r} - \mathbf{R}_P|^2\right) d\mathbf{r},$$

which will depend on the integral kind:

$$\chi_x = \int_{-\infty}^{+\infty} x^2 \exp\left(-2\alpha |x - X_P|^2\right) dx = \left(\frac{1}{4\alpha} + X_P^2\right) \left(\frac{\pi}{2\alpha}\right)^{\frac{1}{2}}.$$

Thus, the generic quadrupole integral might be written as:

$$X_{IJ} = \left(\frac{\alpha}{\pi}\right)^3 \exp\left(-\frac{\alpha}{2} |\mathbf{R}_I - \mathbf{R}_J|^2\right) \left(\frac{1}{4\alpha} + X_P^2\right) \left(\frac{\pi}{2\alpha}\right)^{\frac{3}{2}} = S_{IJ} \left(\frac{1}{4\alpha} + X_P^2\right)$$

and the quadrupole integral in the original kinetic energy contribution can be finally expressed as:

$$Q_{IJ} = S_{IJ} \left(\frac{3}{4\alpha} + |\mathbf{R}_P|^2\right) = \frac{1}{4} S_{IJ} \left(\frac{3}{\alpha} + |\mathbf{R}_I + \mathbf{R}_J|^2\right).$$

Therefore one can write the nuclear kinetic energy expression as:

$$\begin{aligned} K &\equiv \frac{1}{2} |\mathbf{p}|^2 = \hbar^2 \alpha^2 \sum_I \sum_J \mu_{IJ} S_{IJ} \left((\mathbf{R}_I * \mathbf{R}_J) - |\mathbf{R}_I + \mathbf{R}_J|^2 + \frac{1}{4} \left(\frac{3}{\alpha} + |\mathbf{R}_I + \mathbf{R}_J|^2 \right) \right) \\ &= \hbar^2 \alpha^2 \sum_I \sum_J \mu_{IJ} S_{IJ} \left((\mathbf{R}_I * \mathbf{R}_J) + \frac{3}{4} \left(\frac{1}{\alpha} - |\mathbf{R}_I + \mathbf{R}_J|^2 \right) \right) \end{aligned}$$

It is interesting to note that the nuclear density sharpness parameter α in the final expression as shown above, also acts as a scale factor of the nuclear kinetic energy. The final form of the kinetic energy also possess a set of binuclear form factors involving the positions of nuclei in space, which can be manipulated as follows:

$$\begin{aligned} \forall I, J : F_{IJ} &= (\mathbf{R}_I * \mathbf{R}_J) + \frac{3}{4} \left(\frac{1}{\alpha} - |\mathbf{R}_I + \mathbf{R}_J|^2 \right) \\ &= (\mathbf{R}_I * \mathbf{R}_J) + \frac{3}{4} \left(\frac{1}{\alpha} - (|\mathbf{R}_I|^2 + |\mathbf{R}_J|^2 + 2(\mathbf{R}_I * \mathbf{R}_J)) \right) \\ &= \frac{3}{4} \left(\frac{1}{\alpha} - (|\mathbf{R}_I|^2 + |\mathbf{R}_J|^2 + \frac{2}{3}(\mathbf{R}_I * \mathbf{R}_J)) \right) \end{aligned}$$

with this last definition in mind, the final form of the kinetic energy can be written as a sum of three factors, acquiring a simple form:

$$K \equiv \hbar^2 \alpha^2 \sum_I \sum_J \mu_{IJ} S_{IJ} F_{IJ}.$$

7 The LCAO MO density functions as a source of momentum variance

Dilucidated the ASA density function role when evaluating the momentum variance, one can try to find out how the relatively complicated density function structure in LCAO MO theory can be handled in order to obtain the postulated momentum variance and thus the kinetic energy.

The LCAO MO density function can be written in terms of a normalized GTO basis set, usually made of real functions, which here will be expressed as: $\{\chi_{\mu}^I(\mathbf{r} - \mathbf{R}_I) | I = 1, N; \mu = 1, n_I\}$. In a similar manner as in the previous ASA approach, the Latin capital indices mean atomic centers and the Greek indices denote GTO centered at the associated atomic site. In terms of this basis set, the density function can be thus expressed as:

$$\rho(\mathbf{r}) = \sum_{I=1}^N \sum_{J=1}^N \sum_{\mu=1}^{n_I} \sum_{\lambda=1}^{n_J} D_{\mu\lambda}^{IJ} \chi_{\mu}^I(\mathbf{r} - \mathbf{R}_I) \chi_{\lambda}^J(\mathbf{r} - \mathbf{R}_J),$$

where it has been explicitly noted each atomic center, as well as the GTO centered at it. The matrix elements $\{D_{\mu\lambda}^{IJ} | I, J = 1, N; \mu = 1, n_I; \lambda = 1, n_J\}$ are the elements of the *density function coordinates* matrix, a new nomenclature term which has been recently proposed by one of us: [20].

The matrix structure of the coordinates of the density function is essentially a consequence of the form taken when represented in terms of the MO set: $\{\varphi_p(\mathbf{r}) | p = 1, v\}$, and its total dimension can be easily defined via: $v = \sum_{I=1}^N n_I$. In terms of the MO set and the MO occupation numbers: $\{\omega_p | p = 1, v\} \wedge \sum_{p=1}^v \omega_p = N_e$, the density function can be also described as:

$$\rho(\mathbf{r}) = \sum_{p=1}^v \omega_p |\varphi_p(\mathbf{r})|^2.$$

7.1 Postulated momentum structure

Taking into account the GTO basis set derivatives, the postulated momentum in position space could be written as:

$$\mathbf{p} \equiv i\hbar \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) = i\hbar \sum_{I=1}^N \sum_{J=1}^N \sum_{\mu=1}^{n_I} \sum_{\lambda=1}^{n_J} D_{\mu\lambda}^{IJ} \left[\chi_{\lambda}^J(\mathbf{r} - \mathbf{R}_J) \frac{\partial}{\partial \mathbf{r}} \left(\chi_{\mu}^I(\mathbf{r} - \mathbf{R}_I) \right) + \chi_{\mu}^I(\mathbf{r} - \mathbf{R}_I) \frac{\partial}{\partial \mathbf{r}} \left(\chi_{\lambda}^J(\mathbf{r} - \mathbf{R}_J) \right) \right]$$

and obviously enough, the nature of the gradients of the GTO basis set acquire a fundamental role. The gradient vectors, resulting from the derivative involved in the momentum definition, can be accepted as forming another set of vectors, which for simplicity can be named as:

$$\left\{ \mathbf{x}_{\mu}^I(\mathbf{r} - \mathbf{R}_I) = \frac{\partial}{\partial \mathbf{r}} \chi_{\mu}^I(\mathbf{r} - \mathbf{R}_I) | I = 1, N; \mu = 1, n_I \right\},$$

which in turn can be associated with the original GTO basis set to produce a new set of vectors:

$$\forall I, J; \mu\lambda : \mathbf{z}_{\mu\lambda}^{IJ} = \mathbf{x}_{\mu}^I(\mathbf{r} - \mathbf{R}_I) \chi_{\lambda}^J(\mathbf{r} - \mathbf{R}_J).$$

7.2 General description of the gradient of a GTO

Moreover, the gradient of Gaussian functions can be understood as the gradient of a tensor representing a given GTO of any order. In order to construct a mental image about how the gradient relationship with the original GTO structure is made of, one can suppose an unnormalized GTO is represented by the set of the elements of a symmetrical tensor of rank n constructed as follows:

$$\gamma_n(\mathbf{r}|\alpha) = \left(\bigotimes_{p=1}^n \mathbf{r} \right) \gamma_0(\mathbf{r}|\alpha) \leftarrow \gamma_0(\mathbf{r}|\alpha) = \exp(-\alpha|\mathbf{r}|^2).$$

The gradient of the above GTO tensor representation can be easily written as a new tensor of rank $n+1$, by using the algorithm:

$$\frac{\partial}{\partial \mathbf{r}} \otimes \gamma_n(\mathbf{r}|\alpha) = [n\delta(n > 0) \mathbf{I} \otimes \gamma_{n-1}(\mathbf{r}|\alpha) - 2\alpha\gamma_{n+1}(\mathbf{r}|\alpha)],$$

where the symbol $\mathbf{I} = \{\delta_{IJ}\}$ is the second rank unit tensor and $\delta(n > 0)$ is a logical Kronecker's delta, which becomes zero or one, depending upon the included condition becomes false or true, respectively. If the GTO is centered at some point in space, \mathbf{R} say, then it is a matter to use the substitution: $\mathbf{r} \rightarrow \mathbf{r} - \mathbf{R}$ in the above formula.

7.3 Evaluation of momentum variance

The evaluation of the mean momentum is necessarily associated to the calculation of the vector overlap integral involving the three dimensional vectors previously defined:

$$\forall I, J; \mu\lambda : \mathbf{s}_{\mu\lambda}^{IJ} = \langle \mathbf{z}_{\mu\lambda}^{IJ} \rangle.$$

In this way the mean momentum vector could be written as:

$$\langle \mathbf{p} \rangle \equiv i\hbar \left\langle \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) \right\rangle = i\hbar \sum_{I=1}^N \sum_{J=1}^N \sum_{\mu=1}^{n_I} \sum_{\lambda=1}^{n_J} D_{\mu\lambda}^{IJ} \left[\mathbf{s}_{\mu\lambda}^{IJ} + \mathbf{s}_{\lambda\mu}^{JI} \right],$$

and contrarily to the previous examples, now it might happen to be a set of non-null integrals vector. In order to proceed to obtain the variance, now it is needed the squared module of the above expression, thus it can be written:

$$\begin{aligned} |\langle \mathbf{p} \rangle|^2 &\equiv \hbar^2 \left| \left\langle \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) \right\rangle \right|^2 \\ &= \hbar^2 \sum_{I=1}^N \sum_{J=1}^N \sum_{\mu=1}^{n_I} \sum_{\lambda=1}^{n_J} \sum_{P=1}^N \sum_{Q=1}^N \sum_{\alpha=1}^{n_P} \sum_{\beta=1}^{n_Q} D_{\mu\lambda}^{IJ} D_{\alpha\beta}^{PQ} \left[\mathbf{s}_{\mu\lambda}^{IJ} + \mathbf{s}_{\lambda\mu}^{JI} \right] \cdot \left[\mathbf{s}_{\alpha\beta}^{PQ} + \mathbf{s}_{\beta\alpha}^{QP} \right]. \end{aligned}$$

The scalar products between the overlap vectors can be symbolized by a unique completely symmetric scalar symbol:

$$S \left(\begin{matrix} IJPQ \\ \mu\lambda\alpha\beta \end{matrix} \right) = \left[\mathbf{s}_{\mu\lambda}^{IJ} + \mathbf{s}_{\lambda\mu}^{JI} \right] \cdot \left[\mathbf{s}_{\alpha\beta}^{PQ} + \mathbf{s}_{\beta\alpha}^{QP} \right]$$

using it, the squared module of the mean momentum vector can be simply written as:

$$|\langle \mathbf{p} \rangle|^2 \equiv \hbar^2 \sum_{I=1}^N \sum_{J=1}^N \sum_{\mu=1}^{n_I} \sum_{\lambda=1}^{n_J} \sum_{P=1}^N \sum_{Q=1}^N \sum_{\alpha=1}^{n_P} \sum_{\beta=1}^{n_Q} D_{\mu\lambda}^{IJ} D_{\alpha\beta}^{PQ} S \left(\begin{matrix} IJPQ \\ \mu\lambda\alpha\beta \end{matrix} \right),$$

which can be also seen as a quadratic form between the density function coordinates matrix, considered now as a vector: $|\mathbf{D}\rangle = \left\{ D_{\mu\lambda}^{IJ} \right\}$, and the matrix of the scalar products between the overlap vectors: $\mathbf{S} = \left\{ S \left(\begin{matrix} IJPQ \\ \mu\lambda\alpha\beta \end{matrix} \right) \right\}$, that is:

$$|\langle \mathbf{p} \rangle|^2 \equiv \hbar^2 \langle \mathbf{D} | \mathbf{S} | \mathbf{D} \rangle.$$

On the other hand, the mean value of the squared momentum module can be described first by using the squared module written as:

$$\langle |\mathbf{p}|^2 \rangle \equiv \hbar^2 \left\langle \left| \sum_{I=1}^N \sum_{J=1}^N \sum_{\mu=1}^{n_I} \sum_{\lambda=1}^{n_J} D_{\mu\lambda}^{IJ} \left[\mathbf{z}_{\mu\lambda}^{IJ} + \mathbf{z}_{\lambda\mu}^{JI} \right] \right|^2 \right\rangle$$

and then realizing that a similar expression as the squared module of the momentum mean value can be written. Using the vector symbol for the hybrid gradient-orbital products, then there has to be now evaluated a generic integral type as:

$$Z \left(\begin{matrix} IJPQ \\ \mu\lambda\alpha\beta \end{matrix} \right) = \left\langle \left[\mathbf{z}_{\mu\lambda}^{IJ} + \mathbf{z}_{\lambda\mu}^{JI} \right] \cdot \left[\mathbf{z}_{\alpha\beta}^{PQ} + \mathbf{z}_{\beta\alpha}^{QP} \right] \right\rangle,$$

which can be expressed by the sum of a set of four integral terms involving scalar products of the vectors bearing GTO functions and their gradients:

$$Z \left(\begin{matrix} IJPQ \\ \mu\lambda\alpha\beta \end{matrix} \right) = \langle \mathbf{z}_{\mu\lambda}^{IJ} \cdot \mathbf{z}_{\alpha\beta}^{PQ} \rangle + \langle \mathbf{z}_{\mu\lambda}^{IJ} \cdot \mathbf{z}_{\beta\alpha}^{QP} \rangle + \langle \mathbf{z}_{\lambda\mu}^{JI} \cdot \mathbf{z}_{\alpha\beta}^{PQ} \rangle + \langle \mathbf{z}_{\lambda\mu}^{JI} \cdot \mathbf{z}_{\beta\alpha}^{QP} \rangle,$$

where now each one of the four contributions corresponds to another sum of three overlap integrals, involving in turn four center GTO. As a final general result though, one can also write:

$$\langle |\mathbf{p}|^2 \rangle \equiv \hbar^2 \sum_{I=1}^N \sum_{J=1}^N \sum_{\mu=1}^{n_I} \sum_{\lambda=1}^{n_J} \sum_{P=1}^N \sum_{Q=1}^N \sum_{\alpha=1}^{n_P} \sum_{\beta=1}^{n_Q} D_{\mu\lambda}^{IJ} D_{\alpha\beta}^{PQ} Z \left(\begin{matrix} IJPQ \\ \mu\lambda\alpha\beta \end{matrix} \right),$$

which allows the expression of the momentum variance to be compactly written as:

$$\text{var}(\mathbf{p}) \equiv \hbar^2 \langle \mathbf{D} | \mathbf{Z} - \mathbf{S} | \mathbf{D} \rangle,$$

by simply defining the matrix: $\mathbf{Z} = \left\{ Z \begin{pmatrix} I & J & P & Q \\ \mu & \lambda & \alpha & \beta \end{pmatrix} \right\}$ in the same way as the former matrix \mathbf{S} has been defined.

7.4 Evaluation of kinetic energy

Finally, the associated kinetic energy can be easily computed from the quadratic form:

$$K \equiv \frac{\hbar^2}{2m} \langle \mathbf{D} | \mathbf{Z} | \mathbf{D} \rangle.$$

8 Conclusions

A postulate reasonably based on the building of the momentum expectation value in position space has been presented. Such scheme is constructed by means of the customary quantum mechanical momentum operator and the knowledge of the first order density function. This logical outline permits to obtain a coherent Heisenberg uncertainty principle expression for a model density. From there it is possible to describe how to construct momentum vectors in position space from density functions. Once such a construct is set, the expectation values of the momentum, its square and the squared module of the momentum can be easily set up. This last expectation value is directly related with the kinetic energy of the system represented by the known density function. This issue permits to be confident into finding a procedure to compute approximate quantum mechanically based algorithms using approximate density functions. Several examples of momentum construction issuing from diverse density function forms, including the ab initio LCAO MO one, have been presented and fully developed. In all studied cases no insurmountable computational problems appear. The possibility to compute kinetic energy from solely knowing first order density functions seems a feasible characteristic of quantum systems, which can be transformed into some useful computational feature.

Acknowledgments This manuscript was developed while one of us (R. C-D.) was invited professor at the China University of Petroleum - Beijing. The received support from this institution is deeply acknowledged. The authors also want to acknowledge the support of the University of Girona by means of the grant: ASING12/05.

References

1. P.W. Ayers, R.G. Parr, A. Nagy, *Intl. J. Quantum Chem.* **90**, 309–326 (2002)
2. J.S.M. Anderson, P. W. Ayers, J. I. Rodriguez Hernandez, *J. Phys. Chem.* **114**, 8884–8895 (A 2010)

3. D. Chakraborty, P.W. Ayers, Kinetic energy functionals of the electron density and pair density. In *Concepts and Methods in Modern Theoretical Chemistry, vol. 1: Electronic Structure and Reactivity*, eds. S.K. Ghosh, P.K. Chattaraj, (CRC Press, Boca Raton, Florida, 2013), pp. 1–42 (2013)
4. W. Kohn, L.J. Sham, *Phys. Rev.* **140**, A1133A1138 (1965)
5. R. Carbó-Dorca, *J. Math. Chem.* **51**, 420–426 (2013)
6. E. Besalú, R. Carbó-Dorca, *J. Math. Chem.* **49**, 1769–1784 (2011)
7. D. Andrae, *Phys. Rep.* **336**, 413–525 (2000)
8. R. Carbó-Dorca, *J. Math. Chem.* **38**, 671–676 (2005)
9. E. Besalú, R. Carbó-Dorca, *J. Math. Chem.* **51**, 1771–1783 (2013)
10. Ll Amat, R. Carbó-Dorca, *J. Comput. Chem* **18**, 2023–2029 (1997)
11. Ll Amat, R. Carbó-Dorca, *J. Comput. Chem* **20**, 911–920 (1999)
12. Ll Amat, R. Carbó-Dorca, *J. Chem. Inf. Comput. Chem. Sci.* **40**, 1188–1198 (2000)
13. R. Carbó, E. Besalú, B. Calabuig, L. Vera, Molecular quantum similarity: theoretical framework, ordering principles and visualization techniques. *Adv. Quantum Chem.* **25**, 253–313 (1994)
14. R. Carbó-Dorca, E. Besalú, *J. Molec. Struct. Theochem* **451**, 11–23 (1998)
15. R. Carbó-Dorca, Ll. Amat, E. Besalú, X. Gironés, D. Robert, *Quantum Molecular Similarity: Theory and Applications to the Evaluation of Molecular Properties, Biological Activity and Toxicity*. Mathematical and Computational Chemistry: Fundamentals of Molecular Similarity. Kluwer/Plenum Publishers, pp. 187–320 (2001)
16. P. Bultinck, X. Gironés, R. Carbó-Dorca, *Molecular Quantum Similarity: Theory and Applications*; *Rev. Comput. Chem.* vol. 21, Eds. K.B. Lipkowitz, R. Larter, T. Cundari, Wiley, Hoboken, pp. 127–207 (2005)
17. P. Bultinck, S. Van Damme, R. Carbó-Dorca, Molecular quantum similarity, in *Theory of Chemical Reactivity (A Density Functional View)*, ed. by P. Chattaraj (Taylor & Francis, Boca Raton, 2009), pp. 229–242
18. R. Carbó-Dorca, E. Besalú, L.D. Mercado, *J. Comput. Chem.* **32**, 582–599 (2011)
19. R. Carbó-Dorca, Soft Nuclear Density and Nuclear Repulsion. IQCC Technical Report TC-2014-2. *Ind. J. Chem. A* (to be published)
20. R. Carbó-Dorca, *J. Math. Chem.* **51**, 1681–1683 (2013)