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FISHER INFORMATION:
UNCERTAINTY RELATION AND STERIC EFFECT

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Abstract

The Fisher information has a locality property which allows one to quantify the gradient content of the quantum-mechanical states of a physical system, so grasping the distinctive oscillatory character of the corresponding wavefunctions. We discuss the uncertainty relation fulfilled by the position and momentum Fisher information for general systems, and the tighter uncertainty relation satisfied by the eigenfunctions of arbitrary central potentials. Moreover, we show the usefulness of these two quantities together with the measure of the steric effect for the explanation of the origin of the internal rotation barrier between the eclipsed and staggered conformers of ethane.

Keywords: information theory of quantum systems, Fisher information, uncertainty relations, central potentials, steric effect, molecular physics, ethane.

1.   Introduction

In the last few years [1, 2], the information-theory characterization of quantum systems has been shown to be extremely useful to produce new insights into the electronic structure of atoms and molecules, providing a new paradigm to interpret and complement the macroscopic and microscopic properties of atomic and molecular systems derived by recourse to the standard methodologies of quantum theory. The information-theory measures of the single-particle probability density $\rho(\mathbf{r})$ of a quantum system quantify different facets of its internal disorder as described by the spreading of the density over the space. They have been shown that the uncertainty measures are much more appropriate and stringent

than the celebrated variance; e.g., they have been used to obtain mathematical formulations [3–6] of the Heisenberg position–momentum uncertainty principle much stronger than the variance-based Heisenberg–Kennard relation. Most measures (Rényi, Shannon, Tsallis, etc.) have a global character in the sense that they are almost insensitive to the distinctive oscillatory feature of quantum wavefunctions, so to the irregularities or fluctuations of the associated density; this is mainly because they are defined by means of power or logarithmic functionals of $\rho(\mathbf{r})$. They give the extent to which the density is spread over the space in various complementary ways.

There exists an information-theory measure, the Fisher information $F_{\mathbf{r}}$, which has the locality property. It is defined by

$$F_{\mathbf{r}} = \left\langle \|\nabla \ln \rho(\mathbf{r})\|^2 \right\rangle = \int \frac{\|\nabla \rho(\mathbf{r})\|^2}{\rho(\mathbf{r})} d\mathbf{r}.$$

This quantity is the translationally invariant version of the parameter-dependent Fisher information originally introduced by R. E. Fisher [7] in the statistical estimation theory, which has been applied in a great deal of scientific and technological fields [8]. It quantifies the gradient content of the density, so nicely grasping the oscillatory behavior of the concomitant quantum wavefunction. The higher it, the more localized the density, the smaller the uncertainty, and the higher the accuracy in estimating the localization of the particle [8,9].

In contrast to the Shannon entropy, which is a global measure of the spread of the density, the Fisher information may be considered as a measure of its narrowness [10]. Moreover, the Fisher information has been shown (a) to be a good indicator of correlations in atomic systems [11,12] and the most distinctive nonlinear spectral phenomena (i.e., avoided crossings) of atoms in strong external fields [13], (b) to explain the periodicity and shell structure in the periodic table, from hydrogen to lawrencium [14,15], (c) to predict the stationary points and bond breaking/forming regions in chemical reactions [16], (d) to characterize variationally various equations of motion [17], and (e) to rederive the classical thermodynamics without requiring the usual concept of Boltzmann entropy [18].

Let us also mention that the Fisher information is closely related to the kinetic and Weizsäcker energies [10,19]. The latter relation will play here a special role because of its special connection with the steric energy [20].

In this paper, first we use the position and momentum Fisher information to discuss the mathematical formulation of the uncertainty relation for general systems [6] and its improvement for central systems [21–23], which considerably extends the Stam uncertainty inequality [9] (see Sec. 2), and then in Sec. 3 we apply these two quantities to explain the internal rotation barrier between the eclipsed and staggered conformers of ethane [24,25].

2.   Fisher-Information-Based Uncertainty Relation

Until now the only known uncertainty inequality which involves the Fisher information was the 1959-dated Stam inequality

$$F_{\mathbf{r}} \leq 4\langle \mathbf{p}^2 \rangle, \qquad F_{\mathbf{p}} \leq 4\langle \mathbf{r}^2 \rangle$$

for general one-dimensional systems [9, 26, 27] (see [14, 15, 19] for its extension to the three and D-dimensional many-body systems). This relation links the Fisher information in one space with the second-order expectation value in the conjugated space. More than forty years later, the uncertainty

relation between the position-and-momentum Fisher information was discovered for arbitrary central potentials [21–23]. Here we discuss the extension of this result as given by

$$F_{\mathbf{r}}F_{\mathbf{p}} \geq 4D^2, \tag{1}$$

where D is the dimensionality of the system, which is valid for general systems with a real position wavefunction or a real momentum wavefunction, and $F_{\mathbf{p}}$ denotes the momentum Fisher information given by

$$F_{\mathbf{p}} = \int \frac{\|\nabla\gamma(\mathbf{p})\|^2}{\gamma(\mathbf{p})}\, d\mathbf{p},$$

where $\gamma(\mathbf{p})$ denotes the momentum probability density of the system.

To prove (1), we use the following methodology [6].

We have to minimize the Fisher product $G = F_{\mathbf{r}}F_{\mathbf{p}}$ for a normalized-to-unity density. Assuming reality for the momentum wavefunction, we find that $F_{\mathbf{p}} = 4\langle\mathbf{r}^2\rangle$. Then, we realize that the resulting Fisher product is invariant under the linear transform

$$u(\mathbf{r}) \rightarrow u_\lambda(\mathbf{r}) = \lambda^{\frac{D}{2}} u(\lambda\mathbf{r}),$$

where $u(\mathbf{r}) = \sqrt{\rho(\mathbf{r})}$. This invariant property allows us to show that the previous minimization is equivalent to the variational problem

$$\delta\left\{4\int \|\nabla u(\mathbf{r})\|^2\, d\mathbf{r} + \alpha\left[\int u^2(\mathbf{r})\, d\mathbf{r} - 1\right] + \beta\left[\int \mathbf{r}^2 u^2(\mathbf{r})\, d\mathbf{r} - b\right]\right\} = 0,$$

where α and β are the Lagrange multipliers.

It turns out that the associated Euler–Lagrange equations can be recast into the Schrödinger form as follows:

$$-\frac{1}{2}\nabla^2 u(\mathbf{r}) + V(\mathbf{r})u(\mathbf{r}) = -\frac{1}{8}\alpha u(\mathbf{r}),$$

with the quadratic potential $V(\mathbf{r}) = \beta\mathbf{r}^2/8$. Then, the minimizer $u_m(\mathbf{r})$ corresponds to the ground state of $V(\mathbf{r})$, i.e.,

$$u_m(\mathbf{r}) = \frac{1}{\left(\pi^{1/2}a\right)^{D/2}} e^{-\mathbf{r}^2/2a^2}, \quad \text{with } a = \left(\frac{4}{\beta}\right)^{1/4}.$$

Finally, the calculation of the position-and-momentum Fisher information of this function gives the relation (1) in a straightforward manner.

Relation (1), which we have just proved for systems with a real momentum wavefunction, can similarly be shown to be valid for systems with a real position wavefunction. However, we have observed [6] that this is not the universal Fisher-information-based uncertainty relation in the sense that it is not valid for general systems with arbitrary dimensionality. Indeed, although relation (1) is satisfied by a great deal of complex wavefunctions, it is not fulfilled by all complex wavefunctions of general systems.

Finally, let us show that it is possible to find the Fisher-information-based uncertainty relation for general systems provided they are spherically symmetric. To do that, we follow a different methodology which starts with the Schrödinger equation of the central potentials, using the hyperspherical coordinates

$\mathbf{r} = (r; \theta_1; \theta_2; \ldots; \theta_{D-1}) \equiv (r; \Omega_{D-1})$. Then, the quantum states are characterized by the d integer hyperquantum numbers $\{l \equiv \mu_1, \mu_2, \ldots, \mu_{D-1} \equiv m\}$, which may have the values

$$l = 0, 1, 2, \ldots, \qquad l \geq \mu_2 \geq \cdots \geq |\mu_{D-1}|,$$

Then we calculate the position-and-momentum Fisher information in terms of two radial moments, obtaining the values [28]

$$F_{\mathbf{r}} = 4\langle \mathbf{p}^2 \rangle - 2(2l + D - 2)|m|\langle \mathbf{r}^{-2} \rangle,$$
$$F_{\mathbf{p}} = 4\langle \mathbf{r}^2 \rangle - 2(2l + D - 2)|m|\langle \mathbf{p}^{-2} \rangle$$

in the position and momentum spaces, respectively. Now the use of the radial uncertainty inequalities [21–23]

$$\langle \mathbf{p}^2 \rangle \geq \left(l + \frac{D-2}{2} \right)^2 \langle \mathbf{r}^2 \rangle, \qquad \langle \mathbf{r}^2 \rangle \geq \left(l + \frac{D-2}{2} \right)^2 \langle \mathbf{p}^2 \rangle,$$

allows us to find the reverse Stam inequalities

$$F_{\mathbf{r}} \geq 4 \left(1 - \frac{|m|}{2l + D - 2} \right) \langle \mathbf{p}^2 \rangle, \qquad F_{\mathbf{p}} \geq 4 \left(1 - \frac{|m|}{2l + D - 2} \right) \langle \mathbf{r}^2 \rangle.$$

The multiplication of these two inequalities yields the mathematical link between the Fisher product $F_{\mathbf{r}} F_{\mathbf{p}}$ and the Heisenberg–Kennard uncertainty product

$$F_{\mathbf{r}} F_{\mathbf{p}} \geq 16 \left(1 - \frac{2|m|}{2l + D - 2} \right)^2 \langle \mathbf{r}^2 \rangle \langle \mathbf{p}^2 \rangle,$$

which clearly manifests the uncertainty character of the Fisher product. Moreover, taking into account the general Heisenberg–Kennard relation $\langle \mathbf{r}^2 \rangle \langle \mathbf{p}^2 \rangle \geq D^2/4$, or better its improvement for central potentials given by

$$\langle \mathbf{r}^2 \rangle \langle \mathbf{p}^2 \rangle \geq (l + D/2)^2,$$

one finally obtains [21–23]

$$F_{\mathbf{r}} F_{\mathbf{p}} \geq 16 \left(1 - \frac{2|m|}{2l + D - 2} \right)^2 (l + D/2)^2, \tag{2}$$

which provides the Fisher-information-based uncertainly relation valid for all quantum status of any central potential. Note that, for $l = m = 0$, this expression boils down to the uncertainty relation (1) previously discussed.

Finally, for the sake of completeness, let us mention here that the calculation of the Fisher information of the D-dimensional hydrogenic systems yields the values [29, 30]

$$F_{\mathbf{r}} F_{\mathbf{p}} = \frac{8(\eta - |m|)}{\eta} \left[5\eta^2 - 3L(L+1) - (8\eta - 6L - 3)|m| + 1 \right],$$

where $\eta = n + (D-3)/2$ and $L = l + (D-3)/2$, for the Fisher uncertainty product, which certainly fulfills relation (2) of central potentials as expected, since the Coulomb potential is spherically symmetric.

3.　Fisher Information and the Steric Effect: A Study of the Internal Rotation Barrier of Ethane

On the basis of a density-based quantification of the steric effect (i.e., the blocking of access to a reactive site by nearby groups) [25], the origin of the internal rotation barrier between the eclipsed and staggered conformers of ethane has been systematically investigated [24] from the information-theory point of view using the Fisher information measure in conjugated spaces.

In ethane (CH_3CH_3), for example, both carbons are approximately tetrahedral. Thus, there are two limiting structures: staggered ethane, in which the carbon–hydrogen bonds are as far apart as possible, and eclipsed ethane, in which the bonds are as close as possible. These two structures are certainly not the same. There exist two options for the electronic structure calculations of the conformeric study (varying of the dihedral angle of hydrocarbons) — the adiabatic case allows one to optimize the whole geometric structure, whereas in the vertical case the geometry remains fixed (except for the dihedral). Thus, two kinds of computational approaches were considered, adiabatic (with optimum structure) and vertical (with fixed geometry). Our results show that in the adiabatic case the eclipsed conformer possesses a larger steric repulsion than the staggered conformer, but in the vertical cases the staggered conformer retains a larger steric repulsion. Our results verify the plausibility for defining and computing the steric effect in the post-Hartree–Fock level of theory according to the scheme proposed by Liu.

Let us start by recalling the link between the Fisher information $F_{\mathbf{r}}$ and the Weizsäcker $T_w[\rho]$ energy already mentioned in Sec. 1 $T_w[\rho] = (N/8) F_{\mathbf{r}}$, where N is the number of electrons of the molecule. This energy was introduced by C. F. von Weizsäcker as an inhomogeneity correction to the atomic-kinetic-energy density within the framework of the Thomas–Fermi theory of atoms and molecules. This was done for better reproducing the electronic behavior very near and very far from the nucleus, and partial explanation of the very existence of molecules. Moreover, it has been shown [25] that the steric effect $E_S[\rho]$, which is a measure of the intrinsic dimensions upheld by the system with the contributions from other effects (e.g., quantum and electrostatic) completely excluded, is given by the Weizsäcker energy, so that

$$T_w[\rho] = \frac{N}{8} \int \frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})}\, d^3 r. \tag{3}$$

Regarding the behavior of Fisher information, Nagy [20] has pointed out that for a normal distribution, $F_{\mathbf{r}}$ is equal to the inverse variance $V_{\mathbf{r}}$ in Cramer–Rao's inequality $F_{\mathbf{r}} V_{\mathbf{r}} \geq D^2$, with D being the space dimensionality [8,26,27]. In this case, a narrower distribution (a density that extends to a small portion in the space) has a larger Fisher information. On the other hand, if the density fills a large volume in space, the Fisher information is small. Even though atoms and molecules do not possess normal distributions, still Cramer–Rao's inequality holds, and Fisher information represents a measure of the "narrowness" of a distribution, meaning that the steric-energy proposition [25] can be supported by the information-theory arguments.

3.1.　Total and Steric Energies

To investigate the plausibility of defining and computing the steric effect in the post-Hartree–Fock level of theory and assessing its impact on the energy, we have tabulated the steric energies for the aforementioned methods by use of (3) for the staggered and eclipsed conformations of ethane at different levels of theory along with the adiabatic and vertical energy differences (eclipsed-staggered) between the

two conformers. As one can see in Table 1, with each conformer of ethane in the optimized geometry, the steric energy difference for the adiabatic case yields a positive quantity for all methods, indicating the well-known fact that the eclipsed conformer holds a larger steric repulsion than the staggered conformer. In contrast, for the vertical cases where bond distances and angles take either the staggered or eclipsed values, the steric energy differences become negative for all methods, showing that the staggered conformer holds a larger steric repulsion than its eclipsed counterpart. This is not reflected in the total energy differences [24], which are all positive, but in the steric energy ones where the hindrance impediment becomes important, i.e., neglect of the electronic interactions by constraining the geometry in the vertical case (no relaxing effects) causes the nuclear interactions to be more important in the staggered conformation than in the eclipsed one. These observations are again in agreement with the previous work [31], and this is in accordance with our plausibility argument (see above) with respect to employing post-Hartree–Fock methods to compute steric energies, as can be seen in Table 1.

Table 1. Steric Energy (a.u.) Obtained Using (3) for the Staggered and Eclipsed Conformers of Ethane and the Steric Energy Difference (kcal/mol) at Different Levels of Theory in the *aug-cc-PVDZ* Basis Set.

Method	Staggered^a	Eclipsed (a.u.)		Steric Energy Difference (kcal/mol)	
		Adiabatic	Staggered^b	Adiabatic	Vertical
B3LYP	64.273716	64.278574	64.268906	3.05	-3.02
CCSD(T)	64.575113	64.577781	64.569175	1.67	-3.73
MP2	64.574872	64.578404	64.569175	2.22	-3.57
HF	64.581453	64.585931	64.566387	2.81	-9.45

^{a}Staggered conformation in the optimized geometry.
^{b}Eclipsed conformation in the staggered geometry.

3.2. Conformeric Analysis

In this section, we consider the two vertical cases (eclipsed and staggered) where the conformers are constrained to fixed bond lengths and angles according to the eclipsed or staggered optimized structure and, then vary the internal dihedral angle to obtain the conformeric path for each case. All of them were calculated at the *MP2/aug-ccPVDZ* level of theory for the energies and for the Fisher information measures and at the *B3LYP/aug-ccPVDZ* level for the reactivity parameters. Densities were calculated with a relative error of 10^{-5} for the numerically approximated integrations.

The total energies for both the staggered and eclipsed conformations are shown in Fig. 1 at the *MP2/aug-ccPVDZ* level of theory, where the conformeric structures were obtained in each case by constraining the geometry to that of the optimized eclipsed/staggered conformer (as the reference) to attain the staggered/eclipsed conformeric structure by varying the dihedral angle from $0°$ to $180°$ and from $180°$ to $0°$, respectively. As observed in Fig. 1, the energies remain fairly constant when the torsion angle varies up to a point where the energies are maxima at $60°$ for the staggered, and at $120°$ for the eclipsed reference conformations, and then the eclipsed conformeric structure is attained for the former and the staggered one for the latter as the angle augments/diminishes. To understand the energy changes observed in Fig. 1, we recall the imposed geometry constraints which, in the absence of other electronic
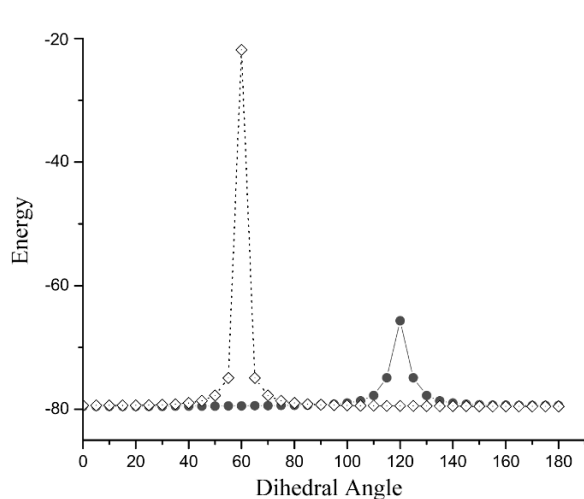
Fig. 1. Total energy (a.u.) for the eclipsed (circles) and the staggered (diamonds) conformations of ethane as the references in the vertical case.
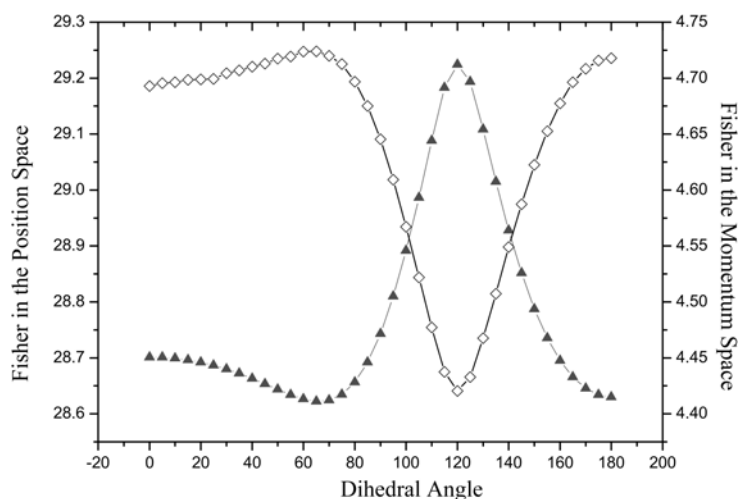
Fig. 2. Fisher information in conjugated spaces (position space in triangles and momentum space in diamonds) for the eclipsed conformation of ethane in the vertical case.

effects arising from the relaxation of the structures, cause the hindrance impediment to be more important in the staggered conformation (of the order of 60 a.u.) than in the eclipsed one (of the order of 15 a.u.) due to the nuclear interactions, i.e., in the former case each hydrogen atom is much more exposed to the rest than in the latter case.

Fisher information in the position and momentum spaces are shown in Fig. 2 at the *MP2/aug-ccPVDZ* level of theory. It may be noted from Fig. 2 that they behave in an opposite manner in accordance with the Heisenberg principle, i.e., Fisher information in the position space shows a local minimum close to $60°$ and a very pronounced maximum at $120°$, and the opposite is observed for the momentum space. Interestingly, both quantities possess richer structure as compared to the energy (see Fig. 1). Concerning the localized/delocalized behavior of the conjugated space densities, we have performed elsewhere [2] an information-theory analysis of the Shannon entropies in conjugated spaces. In the position space, two kinds of structures can be characterized at the extrema of the constrained path for the conformeric eclipsed geometry, i.e., the staggered conformer holds a highly delocalized density at $60°$, whereas the eclipsed conformation possesses a highly localized density at $120°$. In accordance with these features, the Fisher information in the position space is able to measure the "narrowness" of the distributions, i.e., we observe from Fig. 2 that a localized density (squeezing) corresponds to larger values of the Fisher measure whereas a delocalized distribution (less compressed) is associated with smaller values of its gradient. Correspondingly, the staggered conformation constrained to the eclipsed geometry becomes less "compressed" and the eclipsed one more "squeezed," and therefore the influence from the steric effect becomes more pronounced in the eclipsed conformer. The situation for the momentum-space quantities is the opposite, i.e., according to the study of Shannon entropy [2] the staggered conformation shows a localized momentum density (low kinetic energy), whereas a delocalized density in the momentum space is shown for the eclipsed conformation (high kinetic energy), and this is reflected by the Fisher-information quantities as can be seen in Fig. 2, in that a narrow momentum density is observed for the staggered conformation as compared to the eclipsed one, which shows a lesser squeezed density. This behavior altogether shows a picture where the steric effect is shown to be more pronounced for the eclipsed

conformer with a higher kinetic energy and lesser compressed momentum density. A complementary view of the Fisher analysis on the distributions in conjugated spaces can be performed in terms of order/disorder features, i.e., departing from the eclipsed conformation at 0^0 the disorder in the position space augments so as to reach the staggered conformation around $60°$ (minimum for the Fisher measure) and, as the torsion angle varies, a maximum value for the Fisher measure is obtained at $120°$ when the initial conformeric structure is reached, so that its order is maximum. Then, the disorder increases up to an angle of $180°$ when the Fisher measure is minimum, indicating that the staggered conformation has been reached.

4.   Conclusions

In summary, we have analyzed the uncertainty relation (U.R.) of the Fisher information not only for general systems but also for the systems subject to spherically-symmetric potentials. We have found (i) the uncertainty relation for systems with either real position wavefunctions or real momentum wavefunctions and (ii) the uncertainty relation for all wavefunctions of any central potential. Then, more effort is needed to find the universal uncertainty relation satisfying the Fisher information in the position and momentum spaces, i.e., the U.R. valid for all (complex) wavefunctions of arbitrary physical systems. Moreover, we have provided an information-theory-based explanation of the internal-rotation barriers between the eclipsed and staggered conformers of ethane by means of the position-and-momentum Fisher information together with the measure of the steric effect of the molecule.

Note that we have considered two types of rotational barriers: adiabatic (i.e., with optimized geometry) and vertical (i.e., with fixed geometry). We found that the position-and-momentum Fisher information allow us to describe the conformeric path of ethane in the adiabatic and vertical situations when varying the torsion angle to link the localized (delocalized) behavior of the distributions with their narrowness (compression), and hence with the steric effect. The staggered conformer turns out to retain a larger steric repulsion in vertical cases.

Furthermore, we have verified the plausibility of defining and computing the steric effect in a post-Hartree–Fock level of the theory according to the density-functional-based quantification of Liu.

Acknowledgments

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