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A discussion on an apparent MO theory paradox

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A discussion on an apparent MO theory paradox, concerning the probability of positioning a particle within a nodal plane, is carried out in terms of particle confinement probability within finite thickness slabs encompassing the plane in question. It is also discussed how using extended wave functions, the joint position plus kinetic resultant probability distribution, just fulfilling the uncertainty principle, produces a compensating effect on the particle probability of sharing position or momentum within the two half-spaces delimited by the considered nodal plane.

1. Introduction

It is unquestionable that classical MO theory, described many years ago [15], is now a basic form of chemical knowledge, which impregnates the chemical reasoning in such a manner that it will be difficult to ignore today its important role. However, even now some interesting questions arise when MO one-electron functions are analyzed as a source of density functions.

A typical example can be posed in the following way. It is well known that some MO position functions, associated to the quantum chemical structure of planar molecules, the so-called π-type MO, for instance, possess a symmetry plane, which acts as a nodal plane (for a thorough study of the problem and discussion, see, e.g., [9]; for a sequel see [11]). In this molecular nodal plane, $\mathcal{P}$ say, the MO yields a zero value everywhere, that is

$$\forall \mathbf{r}_p \in \mathcal{P} \quad \longrightarrow \quad \psi(\mathbf{r}_p) = 0.$$

This is the equivalent to writing for the attached density function the associated expression

$$\forall \mathbf{r}_p \in \mathcal{P} \quad \longrightarrow \quad \rho(\mathbf{r}_p) = \left|\psi(\mathbf{r}_p)\right|^2 = 0.$$

And this result, apparently, will amount to the same as to let say an electron described by the MO function: $\psi(\mathbf{r})$ has to be confined in either the upper, $\mathcal{P}_{\mathrm{U}}$, or lower, $\mathcal{P}_{\mathrm{L}}$, of the half-spaces defined by the nodal plane, $\mathcal{P}$, because the particle, according to the usual interpretation of quantum mechanics, could never be allowed to traverse an infinite spread slab of zero probability. Such a conclusion presents a contradiction with the fact that the particle has unit probability to be present in the full space.

Statistical arguments, concerning the nature of probability density functions, can be used to better understand the situation [16] and overcome this pretended paradox. Because a probability density function, $\rho(\mathbf{r})$, really represents probability per unit volume, then an isolated point-like density result should be of no value, providing zero probability; that is, formally

$$\mathrm{Prob}(\mathrm{e} \in \mathbf{r}) = 0, \tag{1}$$

where $\mathrm{e} \in \mathbf{r}$ is used to symbolize that the electron is positioned at the point $\mathbf{r}$, while the correct expression to express the probability of finding the particle positioned within an infinitesimal volume element can be easily written as

$$\mathrm{Prob}\bigl(\mathrm{e} \in [\mathbf{r}, \mathbf{r} + \mathrm{d}\mathbf{r}]\bigr) = \rho(\mathbf{r})\,\mathrm{d}\mathbf{r}.$$

Also, it is well known that the following definition holds for a finite volume domain included within the three-dimensional space:

$$\mathrm{Prob}(\mathrm{e} \in V) = \int_V \rho(\mathbf{r})\,\mathrm{d}\mathbf{r}, \tag{2}$$

which becomes unity if V coincides with the whole space.

At a first glance it seems that the particle confinement paradox, performed by the nodal plane, can be a problem of using a probability attachment to the said nodal plane, but without any statistical sense. The following section will try to analyze the situation and find out some plausible extended explanation.

2. The problem analysis for GTO functions

Perhaps, within a statistically correct starting point, the best way to study this apparent nodal plane paradox could be directed to set a question like: “Has it some sense in MO theory to seek for the probability of observing an electron into a sufficiently thick, or thin, surface?”, trying to find a reasonable answer, as well as to discuss the connected result.

At least, in the usual GTO basis set practice [17], the answer can be affirmative under some restrictions. To start, use an origin-centered general Gaussian function directed into the z-axis, for example,

$$\psi(\mathbf{r}) = N_p(\alpha) z^p \exp\bigl(-\alpha|\mathbf{r}|^2\bigr). \tag{3}$$

In this expression, α is the scale factor, $N_p(\alpha)$ is the normalization constant and $p \geqslant 0$ is an integer parameter, which generates a family of GTO functions. The null value of the parameter p corresponds to a spherical nodeless $1s$-type GTO. The next value, $p = 1$, corresponds to a $2p_z$ function with $z = 0$ as the nodal XY plane. Higher parameter values represent higher angular quantum number orbitals, having the same nodal plane characteristic.

The attached probability density function to the GTO, defined in equation (3), is readily constructed as the squared module:

$$\rho(\mathbf{r}) = \left|\psi(\mathbf{r})\right|^2 = N_p^2(\alpha) z^{2p} \exp\left(-2\alpha|\mathbf{r}|^2\right). \tag{4}$$

The probability of an electron lying inside an infinitesimal slab of $2\varepsilon_z$ width, including the XY plane, forming the volume εXY, say, will be readily obtained for the distribution (4):

$$\text{Prob}(\mathrm{e} \in \varepsilon XY) = N_p^2 \left[g_0(2\alpha)\right]^2 \Phi_p(2\alpha; \varepsilon_z),$$

where the function $g_0(2\alpha)$ is related to the Gaussian integral [5]

$$g_p(\alpha) = \int_{-\infty}^{+\infty} u^{2p} \exp\left(-\alpha u^2\right) \mathrm{d}u = \frac{(2p-1)!!}{(2\alpha)^p} \sqrt{\frac{\pi}{\alpha}}, \tag{5}$$

which in turn is a well-known result [17], and $\Phi_p(2\alpha; \varepsilon_z)$ is in general an integral related to the incomplete gamma function and also to the usual error function [1] when $p = 0$. It is defined for convenience here as

$$\Phi_p(a; \xi) = \int_{-\xi}^{+\xi} z^{2p} \mathrm{e}^{-az^2} \, \mathrm{d}z. \tag{6}$$

On the other hand, the squared normalization factor can be written in terms of the above-defined Gaussian integral (5), too:

$$N_p^2 = \left(g_0(2\alpha)\right)^{-2} \left(g_p(2\alpha)\right)^{-1}.$$

Thus, obviously,

$$\text{Prob}(\mathrm{e} \in \varepsilon XY) = \left(g_p(2\alpha)\right)^{-1} \Phi_p(2\alpha; \varepsilon_z), \tag{7}$$

so it can be easily seen how the probability becomes zero as the slab thickness decreases to zero, and tends to 1 at the infinity, when integrals (5) and (6) become equal. The first situation is equivalent to the remark implicit in equation (1), and the second corresponds to the normalization of the function and to the remark of equation (2). This is a normal result coming from the fact of the space dimension reduction, when considering from a single plane up to the whole space. This result will apply almost in the same way when considering any point, axis or plane and the same general function.

In order to have a possible comparison between all cases implicit in the general GTO function, the integral (6) will be developed in a power series, so equation (7) becomes

$$\text{Prob}(\mathrm{e} \in \varepsilon XY) = 2\left(g_p(2\alpha)\right)^{-1} \varepsilon_z^{2p+1} \sum_{k=0}^{\infty} A_k^{(p)} \varepsilon_z^{2k}, \tag{8}$$

where the power series coefficients are defined as

$$A_k^{(p)} = \frac{(-2\alpha)^k}{k!(2(p+k)+1)}.$$

For sufficiently small values of the slab thickness, truncating the series (8) at the first two or three terms will be sufficient to possess a clear probability variation trend, and thus it will be obtained, for example, that

$$\operatorname{Prob}(\mathrm{e} \in \varepsilon XY) \approx 2\bigl(g_p(2\alpha)\bigr)^{-1}\left[\varepsilon_z^{2p+1}\left(\frac{1}{2p+1} - \frac{2\alpha\varepsilon_z^2}{2p+3}\right) + \mathrm{O}\bigl(\varepsilon_z^{2p+5}\bigr)\right].$$

So, from a mathematical point of view, the question of the probability in a plane $z = 0$, that is when $\varepsilon_z = 0$, is trivially answered: it is null, this result being without special statistical relevance. But it will be not so, when a physically thin slab is considered. In fact, in these cases, it will be sufficient to consider an approximation like

$$\operatorname{Prob}(\mathrm{e} \in \varepsilon XY) \approx 2\bigl((2p+1)g_p(2\alpha)\bigr)^{-1}\varepsilon_z^{2p+1}.$$

This expression will permit us to obtain the needed thickness in order to obtain a fixed probability P:

$$\varepsilon_z^{2p+1} \approx \left(p + \frac{1}{2}\right) g_p(2\alpha)P.$$

Inspection of the probability expressed as a power series can provide the following information: in the $1s$-type orbital case, $p = 0$, the probability is directly proportional to the first power of the slab thickness. In other cases, like in p-type GTO or even in higher angular quantum number functions, the density is everywhere vanishing within the nodal plane, usually perpendicular to the function principal symmetry axis. It seems that an extra factor, separating the space in two halves through an almost null probability position plane, is present there. Even one can say that, for the same slab thickness, the overall probability grows smaller as higher angular quantum number functions than in $1s$ GTO are considered.

The probability will decrease swiftly in the neighborhood of the nodal plane in a factor, compared with the $1s$ GTO case, proportional to ε_z^{2p}. So it seems that in higher order angular quantum number functions, possessing nodal planes, the particle position probability decreases in a steepest fashion as the nodal surface approaches, when compared with other functions, which as $1s$-type ones, do not possess such characteristic.

3. Relativistic spinors and classical extended functions

However, in another related field, relativistic quantum mechanics, it is well known that Dirac spinors [2], the relativistic four-component one-electron wave functions, possess a close relationship between large and small components through the momentum operator [13]. For a modern and general discussion of this relationship and the application problems of Dirac equation, see [12]. The result, taken as a whole, appears to provide density functions with probability density in the classical nodal planes, slightly different from classical behavior, when considering the relativistic high angular quantum number functions [14].

Thus, perhaps, the appropriate question to be formulated around this problem is: can within the classical quantum mechanical treatment exist a similar solution to the relativistic case? The answer may be affirmative [12]. Also, an alternative way to study the problem within classical quantum mechanics may consist in taking into account the possibility to construct extended wavefunctions [7] in the form of a vector bearing simultaneously the normalized wavefunction as well as its gradient:

$$\phi(\mathbf{r}) = \begin{pmatrix} \psi(\mathbf{r}) \\ \dfrac{\partial\psi(\mathbf{r})}{\partial\mathbf{r}} \end{pmatrix} = \begin{pmatrix} \psi \\ \nabla\psi \end{pmatrix},$$

such as the corresponding extended density function could be written using an inward matrix product (see, e.g., [3,8]), followed by a complete matrix elements sum (see, e.g., [5,6]):

$$|\phi|^2 = \langle \phi^* * \phi \rangle = \left\langle \begin{pmatrix} \psi^*\psi \\ (\nabla\psi)^*(\nabla\psi) \end{pmatrix} \right\rangle = \left\langle \begin{pmatrix} |\psi|^2 \\ |\nabla\psi|^2 \end{pmatrix} \right\rangle = |\psi|^2 + |\nabla\psi|^2 = \rho + \kappa.$$

This new extended density function is square summable as

$$\int |\phi|^2 \, d\mathbf{r} = \int (\rho + \kappa) \, d\mathbf{r} = 1 + 2K,$$

where K is the kinetic energy expectation value associated to the function $\psi(\mathbf{r})$: $K = \frac{1}{2}\langle \nabla\psi \mid \nabla\psi \rangle$. As a consequence, the extended function can be normalized, and the normalized density function

$$\tau = (1 + 2K)^{-1}(\rho + \kappa)$$

can be seen as a total density function of the system[1]. Such a density function can be interpreted as representing the joint probability of finding the particle within some space volume, V, *or* possessing a certain kinetic energy, K_V, within the same volume. In case of need, the velocity or momentum modules can substitute kinetic energy. The presence of the grammatical particle *or*, translated to the boolean or logical symbol $\vee$, is essential to keep the uncertainty principle valid. So,

$$\mathrm{Prob}(\mathrm{e} \in V \vee \mathrm{e} \in K_V) = \int_V \tau(\mathbf{r}) \, d\mathbf{r}.$$

The joint probability has the chance of having always a summed term, which in a nodal plane bears the characteristic behavior of a function with lesser angular quantum number, in a similar way as in the case when the relativistic spinors are considered.

To visualize this new situation, the already studied general GTO in equation (3) can be chosen again in the extended wave function context. The position density part

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[1] This result and what follows shall be taken in the statistical sense. The physical implications of such a density function are still to be elucidated.

is already discussed, but not the kinetic energy density, which for such a function will need to be based on the gradient elements:

$$\nabla\psi(\mathbf{r}) = N_p(\alpha)\begin{pmatrix} -2\alpha x z^p \\ -2\alpha y z^p \\ p z^{p-1} - 2\alpha z^{p+1}\end{pmatrix}\exp\bigl(-\alpha|\mathbf{r}|^2\bigr).$$

The associated kinetic energy density distribution can be written as

$$\kappa_p(\mathbf{r}) = N_p^2(\alpha)\bigl[4\alpha^2\bigl(x^2+y^2\bigr)z^{2p} + \bigl(p z^{p-1} - 2\alpha z^{p+1}\bigr)^2\bigr]\exp\bigl(-2\alpha|\mathbf{r}|^2\bigr).$$

In the kinetic energy density function above, dealing with a p_z function, i.e. when $p = 1$, a term appears, which bears a $1s$ GTO structure as the one discussed before. The z^4 term could be discarded for the present purpose, as it will provide a still lesser contribution to the probability than the z^2 elements. Thus the kinetic probability compensates the diminution in position probability experienced by a nodal plane MO:

$$\kappa_0(\mathbf{r}) = N_0^2(\alpha)\bigl[4\alpha^2\bigl(x^2+y^2\bigr) - 2\alpha z^2\bigr]\exp\bigl(-2\alpha|\mathbf{r}|^2\bigr).$$

In fact, dropping all the irrelevant terms, for $p > 0$, it can be written when a probability within a slab with small thickness is sought:

$$\kappa_p(\mathbf{r}) \approx \bigl[p N_p(\alpha) z^{p-1}\exp\bigl(-\alpha|\mathbf{r}|^2\bigr)\bigr]^2,$$

or roughly speaking, the result looks as the density of a general GTO function with a power in the variable z one unit less than the generating one.

So, even if in the nodal plane neighborhood, the probability of locating the electron position is small, the probability of finding it with a well-defined momentum may correct the picture in a general manner, at least in a similar way as occurs in lesser angular quantum number orbitals. Thus, even if the probability of the particle being somewhere in the nodal plane neighborhood is small, the probability that in the same region the particle bear a well-defined kinetic energy may compensate the lack of previous information, according to the uncertainty principle.

Moreover, other kinds of extended density functions can be constructed [7], but their use will probably not really add new information to the main results discussed so far. The same can be said with respect to analyzing GTO in spherical coordinates, or other orbital forms, like STO (see, e.g., [18]) or Cartesian STO [4].

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