Localization of electron momentum in atomic and molecular systems

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The problem of localization of atomic and molecular electron momentum is investigated. The atomic systems are studied in terms of the electron momentum localization function (EMLF), a momentum-space counterpart of the electron localization function introduced by Becke and Edgecombe [J. Chem. Phys. **92**, 5397 (1992)]. The shell structure of atoms is better represented by the EMLF than the corresponding radial momentum density and Laplacian of the electron momentum density (EMD). A clear distinction is possible for monotonic and nonmonotonic decreasing atomic EMD's from the EMLF plots. For molecules, the localization is studied via both the Laplacian and the EMLF and are found to be in agreement with each other. The critical structure of the EMD at $p=0$ is represented by the corresponding concentrations and depletions in the Laplacian contour plot.

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I. INTRODUCTION

An important task of a chemist is to understand structure and reactivity of atomic and molecular systems. Among the various means which provide us the information about the structure and reactivity, the one-electron properties such as electron density, electrostatic potentials, etc., form a large domain. Yet another useful one-electron scalar field, which needs greater attention from scientists, is the electron momentum density (EMD). The EMD [denoted here by $\gamma(\mathbf{p})$] is also experimentally accessible via Compton profiles, $(e,2e)$ experiments, etc. [1]. For atomic systems, the EMD studies reveal that unlike the spherically averaged ground-state electron densities, which are monotonic, the EMD can sometimes be nonmonotonic [2]. The shell structure of atoms in $\mathbf{p}$ space has been investigated from the radial momentum density, viz., $4\pi p^2 \gamma(p)$ and is found to have a different structure from the corresponding shell structure in $\mathbf{r}$ space [2]. The shell structure has also been studied via the Laplacian of the atomic EMD, which brings out the localization of the EMD as investigated by Sagar *et al.* [3]. For molecular systems, on the other hand, the effect of bond formation on the EMD has been a subject of great interest. Coulson has investigated this effect for H_2^+ and H_2 molecules and some hydrocarbon systems [4] to propose the famous "bond-directionality principle." Henneker and Cade [5] and Ramirez [6] studied the difference EMD, i.e., $\Delta\gamma(\mathbf{p})=\gamma_{\text{mol}}(\mathbf{p})-\sum_A \gamma_A(\mathbf{p})$, where A are "atoms in the molecule." Recently, Gadre, Limaye, and Kulkarni [7] and Defranceschi and Berthier [8] have investigated symmetry properties of molecular EMD's. Furthermore, Kulkarni, Gadre, and Pathak [9] have studied the topographical characteristics of molecular EMD's as against the corresponding separated atom EMD's to bring out the effects of bonding. These topographical studies have led Kulkarni and Gadre [10] to monitor the progress of chemical reactions using the EMD and the Laplacian of the EMD at zero momentum as an investigative tool. However, detailed studies on the localization of EMD's in molecular systems are yet to find a place in the chemical literature.

In the position space, the effect of bonding in molecules can be brought out through topographical studies of electron densities [11]. The localization of the electron density in the molecule can be studied directly through the Laplacian of the electron density to observe concentrations as well as depletions of that scalar field. The localization of electrons is fundamentally related to the Fermi hole, which has led Luken and co-workers [12] to define the Fermi-hole mobility function. Recently, Becke and Edgecombe [13] proposed a measure of electron localization in terms of the electron localization function (ELF) to bring out the features corresponding to the structure of the molecule, viz., bond, lone pair, etc. Moreover, the shell structure of atoms can be better explained by the ELF as compared to $\nabla^2\rho(r)$, where $\rho(r)$ is the electron density. The ELF (denoted here by F_{EL}) is defined as

$$F_{\text{EL}}=1/[1+(D_\sigma/D_\sigma^0)^2] , \qquad (1)$$

where $D_\sigma^0=\frac{3}{5}(6\pi)^{2/3}\rho_\sigma^{5/3}$ and $D_\sigma=\sum_{i=1}^\sigma|\nabla\psi_i|^2-(\nabla\rho_\sigma)^2/4\rho_\sigma$. The fundamental advantage in using the ELF is that it is bound between 0 and 1. In addition, it exhibits the structural features similar to that of $\nabla^2\rho(\mathbf{r})$ and the Fermi mobility function. Further, Savin *et al.* [14] have utilized the ELF for explaining bonding features in several molecular systems. The solid-state structure of the diamond has also been investigated using the ELF [15]. Recently, Gadre, Kulkarni, and Pathak [16] have proposed a density-based electron localization function by means of which one can probe the localization of electrons in atoms and molecules exclusively from the knowledge of electron density.

In view of the above studies, it is felt to be instructive to ask the following questions about the ground-state electron momentum densities. Which are the regions where the EMD's are localized or which momenta are preferred by the electrons in atoms and molecules? Does there exist any simple p-space function giving the exact

shell structure? Does the localization of the electron momentum density observed through an analogously defined electron momentum localization function (EMLF) exhibit features similar to $\nabla^2\gamma(\mathbf{p})$ for atoms and molecules? Section II answers these questions and compares the shell structure of atoms obtained through $\nabla^2\gamma(p)$ by Sagar et al. [3] with the corresponding EMLF for some closed shell atomic systems. Section III presents discussion on both $\nabla^2\gamma(\mathbf{p})$ and the EMLF for some simple molecular systems.

II. ELECTRON MOMENTUM LOCALIZATION FUNCTION FOR ATOMS

The investigations of the Laplacian of the atomic EMD reveals a rather interesting aspect of shell structure. Sagar et al. [3] computed $\nabla^2\gamma(p)$ (we use $\nabla = \nabla_p$ henceforth) for several neutral and singly positive ions and, based on the occurrence of zeros in it, classified them into seven distinct types. These zeros can be in some cases correlated to the presence of shells, and the values of corresponding p are related to the Bohr's radii in the atomic systems. Moreover, nonmonotonicity in the ground-state EMD is reflected in terms of the positive Laplacian at $p = 0$, whereas the monotonic decreasing EMD leads to negative $\nabla^2\gamma(p)$. In the preceding section the electron localization function (ELF) has been defined. Analogously, one can define a momentum-space ELF, viz., the electron momentum localization function (EMLF), and compare the results with the Laplacian of the corresponding EMD. In case of the EMLF an important restriction is that it can be defined only for closed shell atomic and molecular systems, due to which atomic systems investigated here are Be, Ne, Mg, Ar, Ca, and Kr. The EMLF at each point is obtained analytically using near Hartree-Fock wave functions due to Clementi and Roetti [17].

First we note that the EMLF for two-electron systems is identically unity. The plots for the atoms with completely filled shells, i.e., Ne, Ar, and Kr, are given in Fig. 1. The EMLF plot of the neon atom shows two distinct regions, the first one between $0 \leq p \leq 4.0$ a.u., the second one being form $5.8 \leq p \leq \infty$, and one small shoulder region in between these two regions. Due to the reciprocal nature of the $\mathbf{r}$ and $\mathbf{p}$ spaces, the small-p region corresponds to the valence region in coordinate space; thus the first region pertains to the L shell, the second region is due to the K shell, and the shoulder region might be due to the intershell (subshell) electron momenta of $2s$ electrons. In the case of argon, three such regions are observed corresponding to M, L, and K shells, respectively, and between L and M regions a shoulder is observed corresponding to the intershell maximum, which is caused by filled $2s$ and $3s$ orbitals. For krypton, four regions in the EMLF plot are discernible, along with two shoulders. Moreover, it can be seen from Fig. 1 that Ne, Ar, and Kr have the EMLF < 1 at $p = 0$, which can be attributed to the nonmonotonicity of the corresponding EMD leading to the depletion of the EMD or the positive Laplacian around $p = 0$. This is in contrast with the few more atoms studied here, viz., Be, Mg, and Ca. The plots of the EMLF against p for these atoms are displayed in Fig.
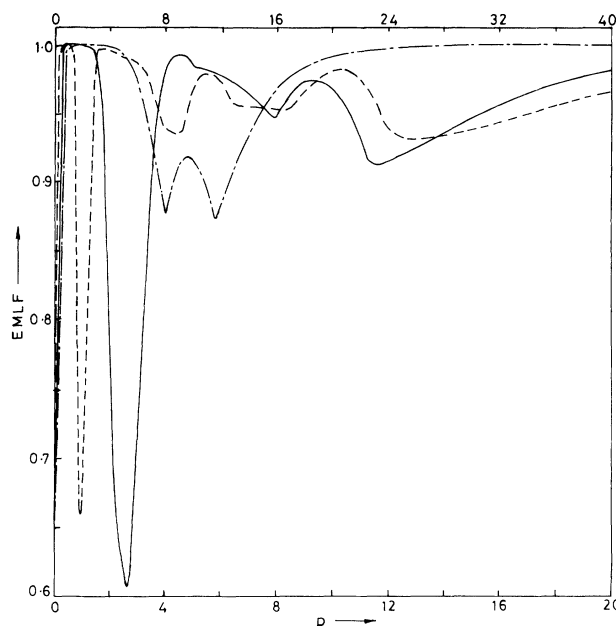

FIG. 1. Plot of the EMLF against p in a.u. for the Ne (— — —), Ar (———), and Kr (— — — —) atoms. The upper scale between $p = 0.0$ to 40.0 a.u. is for the Kr atom.

2. For these atoms, the EMLF value at $p = 0$ indeed attains a maximum, i.e., the EMLF $= 1.0$. This can be related to the monotonic decreasing nature of the EMD of these atoms leading to concentration of the EMD (or the negative Laplacian) around $p = 0$. In Fig. 2, two regions are seen for the beryllium atom, whereas three regions with one shoulder for magnesium and four regions with
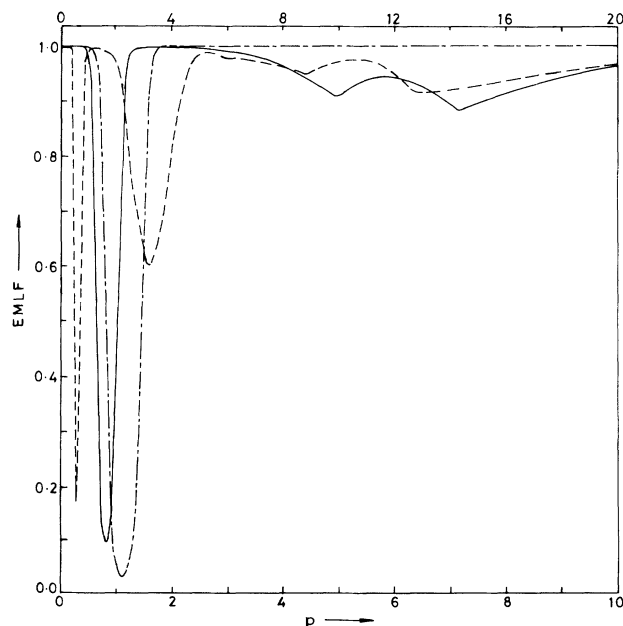

FIG. 2. Plot of the EMLF against p in a.u. for the Be (— — — —), Mg (———), and Ca (— — — —) atoms. The upper scale between $p = 0.0$ to 20.0 a.u. is for the Ca atom.

one shoulder for calcium are observed. This may be said to be a signature of the shells and intershells depicted in the momentum space. Thus, analogous to the ELF in r space, the EMLF describes the shell structure of atoms in p space in a better way than the radial momentum density [2] and $\nabla^2\gamma(p)$ [3].

It may be noted from Figs. 1 and 2 that the EMLF tends to its saturation value of unity asymptotically. This can be explained from the form of the EMLF given in Eq. (1). In the definition of the EMLF we have a ratio of D_σ to D_σ^0, as p tends to infinity, D_σ approaches zero more rapidly as compared to D_σ^0, leading to the EMLF value of unity.

Having described the electron momentum localization and shell structure in p space for atoms, it would be instructive to investigate the localization of electron momentum using the Laplacian as well as the EMLF for molecules. This has been taken up for some simple molecular systems in the next section.

III. ELECTRON MOMENTUM LOCALIZATION IN MOLECULES

As discussed in Sec. I, the measurement of the electron momentum localization can be either in terms of the Laplacian of the EMD or by investigation of the EMLF. For this analysis, the molecules studied are two electron systems, viz., H_2, HeH^+, 10-electron systems like CH_4, NH_3, H_2O, HF, and 18 electron molecules like HCl, F_2, CH_3OH, CH_3F, and C_2H_6. Moreover, the molecules LiH, LiF, HCN, and BF are also studied. The wave functions for these molecules are generated from the program INDMOL [18] using a 6-31G^{**} basis set or $(11s,4p,1d/4s,1p)$ contracted to $[4s,2p,1d/2s,1d]$, i.e., (A 6-31G^{**} atomic basis has polarization of p and d functions added to hydrogen and other second row elements, respectively). The derivatives of the momentum-space wave function as well as the EMD are obtained analytically to compute the EMLF [cf. Eq. (1)].

The topographical features of the EMD of the above chosen set of molecules has been reported by Kulkarni and co-workers [9]. The two-electron molecules such as H_2 and HeH^+ are known to have a maximum, i.e., a $(3,-3)$ type critical point (CP) for $\gamma(p)$ at $p=0$. [The clarification for the $(3,-3)$ critical point may be found in Refs. [9], [10], and [11]. The notation used here is (R,s), where R is rank of Hessian matrix and s denotes excess of positive eigenvalues over the negative ones.] Due to this critical point the contour plots of $\nabla^2\gamma(p)$ of these molecules in the p_x-p_z plane (here z is the bonding axis) exhibit a negative $\nabla^2\gamma(p)$ around $p=0$ (cf. Fig. 3). For both of these molecules the negative Laplacian region is oval shaped around the p_z axis demonstrating the well-known bond-directionality principle [4]. As shown in Fig. 3 for H_2, $\nabla^2\gamma(p)$ is highly negative near $p=0$; thereafter it monotonically increases, passing through zero and subsequently becoming positive. Thus there are two distinct regions of the negative and positive Laplacian, one within the other respectively, and the positive region extends throughout up to infinity. The Laplacian of the EMD for
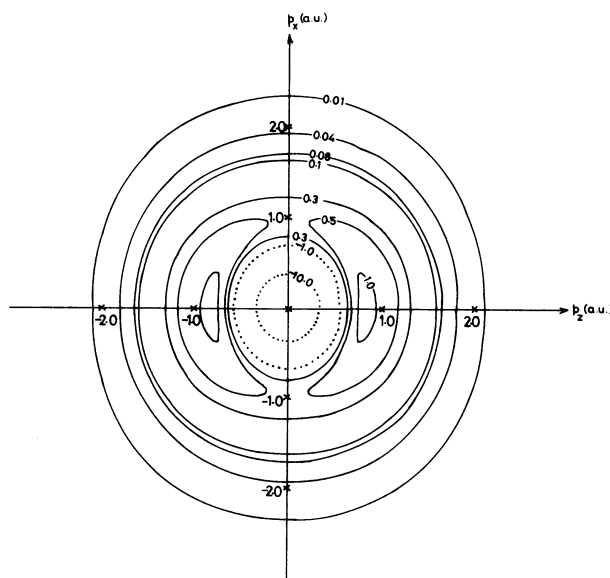

FIG. 3. Contour plot of the Laplacian of the electron momentum density for the H_2 molecule in the p_x-p_z plane. All values are in a.u.

two-electron systems are seen to attain a zero value in every direction away from the origin only once. A close look at the $\nabla^2\gamma(p)$ of ten-electron systems like CH_4, NH_3, H_2O, and HF reveals further interesting structure. All these molecules have a minimum at $p=0$ in their EMD leading to the positive region of $\nabla^2\gamma(p)$ around the origin (cf. Fig. 4 for the CH_4 molecule). The plot clearly shows three distinct regions. The innermost region has the positive Laplacian indicating the depletion of the EMD around $p=0$; this region is engulfed by a negative region pertaining to the concentration of the EMD away from $p=0$ in every direction. This region extends up to
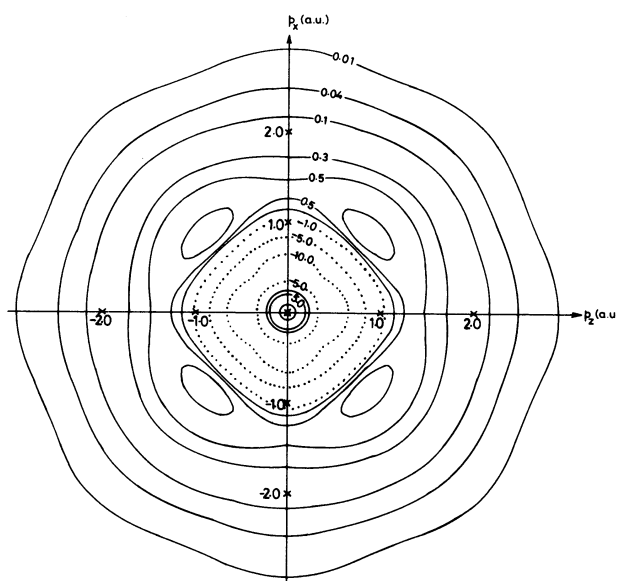

FIG. 4. Contour plot of the Laplacian of the electron momentum density for the CH_4 molecule in the p_x-p_z plane. All values are in a.u.

$|\mathbf{p}| = 1.2$ a.u. and thereafter becomes positive in every direction. Thus, for the ten-electron systems studied herein, the Laplacian attains zero value twice in every direction away from the origin. This is a remarkable feature of retaining atomic shelllike structure in *three dimensions* as one goes from atoms to molecules. In the case of CH_4, the maximum concentration is seen around $|\mathbf{p}| = 0.4$ a.u., whereas the maximum depletion is around the origin. This clearly indicates that the electron momenta less than the average momentum are preferred in the valence region of the molecule (as per the reciprocity demanded from the Fourier transform principle). For ten-electron molecules the electron momenta in the range of $0.3 \le |\mathbf{p}| \le 1.1$ a.u. are highly preferred by attaining the negative Laplacian of the EMD in that region. The momenta corresponding to the localization and depletion indicate anisotropies in the molecular EMD's.

In the case of 18-electron molecules like HCl, having a minimum for the EMD at the origin (cf. Fig. 5), the zero value of $\nabla^2\gamma(\mathbf{p})$ is attained three times away from the origin. This can be attributed to the presence of shell structure in molecules since the chlorine atom is dominant in this molecule. However, this feature is not a general one as can be seen from the $\nabla^2\gamma(\mathbf{p})$ plots of F_2, CH_3OH, CH_3F, and C_2H_6 molecules (not presented here due to paucity of space). The maximum concentration of the EMD for HCl is near $|\mathbf{p}| \sim 0.5$ a.u., whereas the EMD is highly depleted around the origin.

LiF, BF, and HCN molecules show rather complex structure in their $\nabla^2\gamma(\mathbf{p})$ plots. The Laplacian of these molecules show regions of depletion or concentration at $\mathbf{p}=0$ according to the presence of the critical structure of the EMD. A general feature exhibited by all the molecules is that, asymptotically, $\nabla^2\gamma(\mathbf{p})$ reach zero from the positive side. This has been established rigorously for atoms and spherically averaged EMD's by Sagar *et al.* [3].
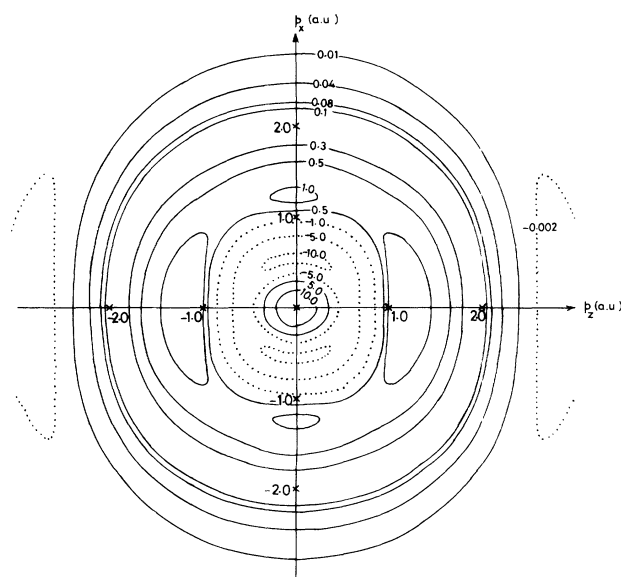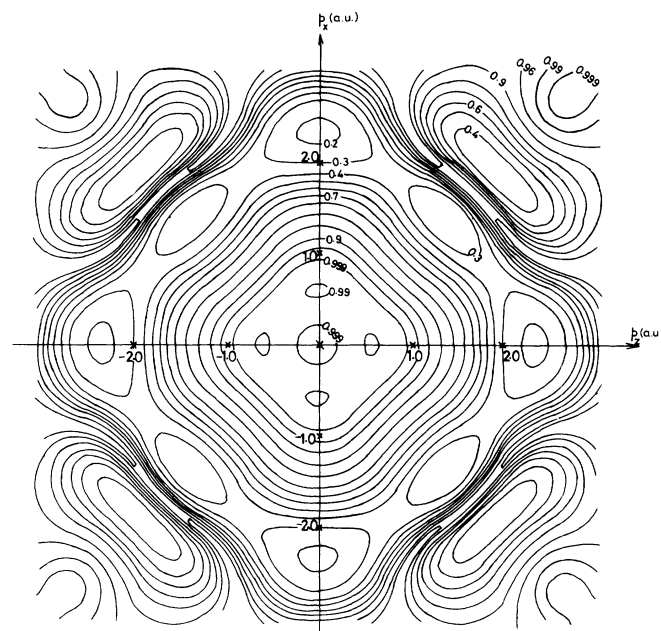

FIG. 6. Contour of the electron momentum localization function for the CH_4 molecule in the p_x-p_z plane. All values are in a.u.

After investigating the structure of the Laplacian of the EMD, it would be interesting to look at the features of the EMLF for the above molecules by way of comparison. It is well known that for two-electron systems the EMLF=1.0 throughout and hence cannot be compared. For ten-electron systems like CH_4 the EMLF plot (cf. Fig. 6) shows localization in the range $0.3 \le |\mathbf{p}| \le 1.0$ a.u. and, thereafter the EMLF decreases outwards. The high EMLF values (EMLF=0.99) are observed around $|\mathbf{p}| \sim 1.0$ a.u. for all ten-electron molecules. The contours of values greater than 0.99 may be observed within this region. Due to depletion of the EMD at $\mathbf{p}=0$, no contours are observed near the origin. However, for molecules like BF and HCN, contours are indeed observed near the origin, implying concentration of the EMD in that region. For 18-electron molecules like HCl, due to the minimum at $\mathbf{p}=0$, the EMLF contours move outwards from the origin and are observed around $|\mathbf{p}| \sim 0.4$ a.u. The comparison of all the EMLF plots with the corresponding $\nabla^2\gamma(\mathbf{p})$ ones revealed that the regions of concentration of the EMD depicted in the $\nabla^2\gamma(\mathbf{p})$ plots are represented by increasing the EMLF values, with depletion represented by lowering the EMLF. Both the EMLF and $\nabla^2\gamma(\mathbf{p})$ are seen to retain the symmetry features of the molecules in momentum space. Thus the information of the localization of the electron momenta obtained from both scalar fields is indeed supplementary.

IV. CONCLUDING REMARKS

The localization of the EMD is investigated in terms of the Laplacian of the EMD and via defining the electron momentum localization function (EMLF) for atoms and molecules. The atomic shell structure is better represented by the EMLF when compared with the corresponding

FIG. 5. Contour plot of the Laplacian of the electron momentum density for the HCl molecule in the p_x-p_z plane. All values are in a.u.

radial momentum density and Laplacian of the EMD. The features of inter-shell orbitals are in terms of the shoulder regions in the EMLF plots. Thus this provides an affirmative answer to the question of a better p-space model representing shell structure. Moreover, the behavior of the EMD at the origin is also represented correctly in terms of the EMLF, due to which the monotonic and nonmonotonic structure of the atomic EMD is identified. For molecular systems, features of both the EMLF and $\nabla^2 \gamma(\mathbf{p})$ are found to be supportive of each other. The critical structure of the EMD at $\mathbf{p}=0$ gets reflected in the corresponding Laplacian and EMLF plots in terms of concentration or depletion. The concentration of the EMD around $\mathbf{p}=0$ implies that the lower momenta, as compared to the average ones, are preferred in the molecule. The preference for higher momenta in some molecules is represented by the depletion of the EMD Laplacian around $\mathbf{p}=0$. Similar structural information is obtained from the study of the molecular EMLF. However, since the EMD is a slowly decreasing function ($\sim p^{-8}$ asymptotic decay), the regions of the EMLF <0.9 should be termed depleted regions when compared with the corresponding Laplacian plots. Both the $\nabla^2 \gamma(\mathbf{p})$ and EMLF retain the symmetry features of the molecular EMD and the anisotropies in the molecular EMD's are brought out well from the contour plots.

For speculating a general case of any complex molecule, if the information regarding its Laplacian of the EMD or its EMLF is obtained by any means, then it is possible to visualize the topographical features of the EMD. This can be achieved by investigating the structure of these two scalar fields near the origin. If the Laplacian shows depletion near the origin, then there is either a minimum or $(3,+1)$-type CP at the origin. As per the earlier studies [9], a consequence of this is that if a minimum is found at the origin then, due to the hierarchy principle, CP's of higher order, i.e., $(3,+1)$, $(3,-1)$, and $(3,-3)$, occur away from the origin. The total number of CP's is limited by the Poincare-Hopf relation [9]. Similarly, if the Laplacian exhibits concentration near the origin, either a $(3,-1)$ or a $(3,-3)$ CP will occur at the origin. Apart from these facts, any *a priori* general prediction about the structure of the Laplacian or EMLF and, in turn, the EMD topography of a molecule is not possible. The main hurdle is that there are no definite signatures of structural parameters like nuclei, bonds, and lone pairs, etc., in the momentum space. Therefore, more studies are warranted to harness this information from the momentum space properties and scalar fields.

In summary, a preliminary study of the localization of the electron momentum density for atoms and molecules is presented. A more elaborate study to understand the role of the EMD concentrations and depletions in bond formation will be taken up for some simple diatomic molecular systems over a wide range of nuclear separations. Moreover, the study of chemical reactions in the framework of the EMD Laplacian or the EMLF will also be rather appealing.

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