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Topographical view of molecular electron-momentum densities

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Topographies of ground-state electron-momentum densities (EMD's), $\gamma(\mathbf{p})$, are studied for a number of diatomic as well as polyatomic molecules and compared with the corresponding separated atom-momentum densities with a view to bring out clearly the effect of bonding from a momentum-space standpoint. All possible critical points of rank three are seen to occur in the molecular EMD topology. Some linear molecules, in particular, are seen to possess a ring of stable critical points. Diatomic molecules constituted of atoms with exclusively s-type orbitals exhibit, in their $\gamma(\mathbf{p})$ topography, a maximum at $\mathbf{p}=\mathbf{0}$. Whenever for any di- or polyatomic system $\gamma(\mathbf{0})$ is maximal, it turns out to be a unique critical point, whereas for all other cases of criticality at $\mathbf{p}=\mathbf{0}$ a definite hierarchy, dictated solely by the criticality at the origin, in the nature of critical points elsewhere is observed. Criticality at $\mathbf{p}=\mathbf{0}$, while being imperative, is seen to have a direct bearing on the anisotropies in EMD that manifestly are chiefly characteristic of molecular, rather than separated-atom, EMD. Further, from studies carried out on some isoelectronic series of diversified polyatomic systems, a correlation between the curvatures associated with the $\mathbf{p}=\mathbf{0}$ criticality and distribution polarity is discovered.

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I. INTRODUCTION

Atomic and molecular electron-momentum densities (EMD's) $\gamma(\mathbf{p})$ have been a subject of considerable interest to chemists for the past 50 years. The molecular EMD is experimentally tractable in that it can be derived from directional Compton profiles [1], which fact endows merit to its study. On the theoretical side, following the pioneering work of Coulson [2], as a result of several studies from different standpoints, the following principles emerged, as categorized by Epstein and Tanner [1]: (1) Fourier-transform principle, (2) virial-theorem principle, (3) bond-directionality principle, (4) bond-oscillation principle, (5) hybrid-orbital principle, and (6) expectation-value principle. In spite of a large number of theoretical as well as experimental investigations, the EMD has eluded a direct interpretation in simple chemical terms and hence has not been much utilized by practicing chemists for furthering their knowledge of molecular structure.

The bond-directionality (BD)principle, which has been a subject of discussion for many years and has recently been very carefully analyzed by Tanner [3], states that "in a chemical bond in a bound molecule in its equilibrium configuration, there are values $\mathbf{p}_m$ of momentum which are more probable, i.e., which correspond to local maxima of $\gamma(\mathbf{p})$. These values are determined by both the geometric and electronic symmetries of the molecule. For momenta $\mathbf{p}=\mathbf{p}_m+\delta\mathbf{p}$ near a maximum, it is more likely that $\delta\mathbf{p}$ is perpendicular rather than parallel to the bond axis." The BD principle, which gives a signature of bonding within the molecular-orbital framework, is clearly operative for covalently bonded diatomic molecules [1–3] and cannot be directly extended to describe polyatomic systems. This follows from the fact that there is no reference to nuclei in the momentum space and that the symmetry of the molecular EMD is enhanced in general as compared to its $\mathbf{r}$-space molecular symmetry [4]. Thus, for polyatomic molecules, with the absence of a straightforward extension of the BD principle, implications of chemical bonding as viewed in the momentum space even at a gross level are difficult to describe and are not reflected in molecular EMD maps. Further, anisotropies in EMD are also not clearly discernible [5–10] (Refs. [5]–[10] are representative studies; for a detailed bibliography, consult Ref. [3]).

Langhoff and Tawil [5] computed the anisotropies in the EMD in terms of those given by the corresponding directional Compton profiles, the latter defined as $J_{\hat{\mathbf{k}}}(q)=\int\gamma(\mathbf{p})\delta(q-\hat{\mathbf{k}}\cdot\mathbf{p})d^3p$, where $\hat{\mathbf{k}}$ is the unit vector in the direction of momentum transferred to the electron, and q is the projection of the momentum-transfer vector on the initial electron-momentum vector. For diatomic and planar molecules, the deviations from sphericity, viz., $J_{\perp}-J_{\mathrm{av}}$ and $J_{\parallel}-J_{\mathrm{av}}$, together qualify to be a good measure of the anisotropies. Here $J_{\perp}$ denotes Compton profile perpendicular to the bond (for diatomics) or to the plane of the molecules (for planar molecules), $J_{\parallel}$ the Compton profile in the direction of the bond or in the plane of the molecules, and J_{av} the spherically averaged Compton profile defined as $J_{\mathrm{av}}(q)=(4\pi)^{-1}\int J_{\hat{\mathbf{k}}}(q)d\Omega_{\hat{\mathbf{k}}}$. Further, for diatomics, Koga, Nakao, and Hao [6] defined the anisotropies in the EMD by $Q_n=\langle p_x^n\rangle/\langle p_z^n\rangle$, where p_x and p_z, respectively, denote perpendicular and parallel components of $\mathbf{p}$. Koga, Nakao, and Hao [6] also argued that the oscillations in the EMD, anisotropies in the molecular EMD, as well as bond polarity, are connected to anisotropies in the molecular kinetic energy. Earlier, Ramerez and co-workers [7] had proposed a measure of "relative anisotropies" in directional Compton profiles in terms of just a single number, namely, the difference between directional Compton profiles at zero momentum, i.e., $\Delta J(0)=J_z(0)-J_x(0)$. Further, Thakkar *et al.* [8] studied anisotropies in the EMD for linear molecules by suitably partitioning it in a Legendre-series expansion. This partitioning is accomplished by expanding

$$\gamma(\mathbf{p})=\gamma_0(p)+\gamma_2(p)P_2(\cos\theta)+\gamma_4(p)P_4(\cos\theta)+\cdots ,$$

where $P_L(\cos\theta)$ are the Legendre polynomials of order L, $\gamma_0(p)$, which is isotropic, gives the spherically averaged EMD, and the products of $\gamma_2(p),\gamma_4(p),\gamma_6(p),\ldots$ with the corresponding P_L's give the anisotropic contribution to the EMD. This expansion is an important step in the partitioning of the EMD to study its anisotropy directly; however, it has been applied only to linear molecules (for polyatomics, the spherical harmonics must be employed). Following this work, Simas, Smith, and Thakkar [9] studied the effect of substituents on the EMD of linear molecules via the Legendre-series partitioning and correlated the substituent constants to the kinetic-energy anisotropies for a given compound, relative to the nonsubstituted parent compound. More recently, Anchell and Harriman [10] have studied the phase-space density using the Husimi function [10] and introduced the concept of local anisotropies in the molecular EMD via the second moment of the momentum tensor that exhibits gross similarities with the results of kinetic-energy anisotropies studied before by Thakkar, Sharma, and Koga [11]. The generalized bond-directionality principle then emerges, as is brought out in Ref. [10]: A plane of three atoms have momenta preferred in a direction normal to the plane. This principle is demonstrated for the H_2O, NH_3, and CH_4 molecular species [10].

While the electron-momentum distribution eludes a direct interpretation, its much studied coordinate-space counterpart, viz., the electron density $\rho(\mathbf{r})$, gives a rather simple picture of molecular bonding in accordance with general chemical intuition and hence is relatively easier to interpret. The salient features of molecular bonding and structure at the microscopic level are customarily obtained by studies on the redistribution of electron densities upon molecule formation and other allied quantities such as electron-density differences maps, force constants, dipole moments, molecular electrostatic potentials, etc. Among these studies, a significant contribution due to Bader [12] is noteworthy, viz., the topological studies of molecular systems in terms of a careful analysis of the molecular electron density $\rho(\mathbf{r})$ itself. Studies on the gradient field and Laplacian of the electron density lead to a useful quantification of terms such as a rigorous definition of atoms in a molecule [12], the chemical bond, and different geometrical structures [12] such as ring systems, cages, and so forth. The study of $\nabla^2\rho(\mathbf{r})$ has provided a firm footing to the concepts of electrophilic and nucleophilic attacks, reactivities, and also to more popular concepts such as hyperconjugation [12]. All these studies essentially hinge on a critical-point analysis of $\rho(\mathbf{r})$ as well as that of $\nabla^2\rho(\mathbf{r})$ and, by means of catastrophe theory as applied to the very concept of stability of molecular structure, endow indeed a new perspective to molecular-structure theory [12].

It is the aim of the present study to point out that the molecular electron- *momentum* density is yet another important scalar field which can be studied in the above perspective, as initiated by Gadre, Limaye, and Kulkarni [4]. Analogous to their position-space counterparts, the momentum-space densities were also studied in terms of difference EMD maps [13], bringing out the effect of molecular-bond formation. In this work we propose to investigate, in fuller detail, the topography of EMD's of some sample molecular systems vis-à-vis those of their corresponding separated-atom-momentum densities and the effect due to molecule formation on the redistribution of $\gamma(\mathbf{p})$ topography. This will enable one to interpret anisotropies in the molecular EMD (through its topographical analysis) directly and seek connections within the phenomenon of chemical bonding. All the analysis carried out here refers to ground-state quantities with atomic units used throughout.

II. TOPOGRAPHY OF MOLECULAR ELECTRON-MOMENTUM DENSITY

The one-electron-molecular electron-momentum density is derived from the N-electron momentum-space wave function $\phi(\mathbf{p}_1,\mathbf{p}_2,\ldots,\mathbf{p}_N)$ as

$$\gamma(\mathbf{p})=N\int|\phi(\mathbf{p},\mathbf{p}_2,\ldots,\mathbf{p}_N)|^2 d^3p_2\cdots d^3p_N , \qquad (1)$$

where $\phi(\mathbf{p}_1,\mathbf{p}_2,\ldots,\mathbf{p}_N)$ is a $3N$-dimensional Fourier-Dirac transform of the coordinate-space molecular wave function $\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$. We have studied the EMD topography for the systems, H_2, CO, BF, N_2, HF, HCN, H_2O, NH_3, CH_4, BH_3, C_2H_2, C_2H_4, C_2H_6, N_2H_4, H_2CO, CH_3OH, CH_3F, C_2H_4O, CH_4N_2, C_2H_5N, C_3H_6, and C_4H_6 using the molecular geometry and basis-set data due to Snyder and Basch [14]. For the species Li_2, LiH, and LiF (using a 3-21G basis), OH^-, CN^-, and N_3^- (with a 4-31G basis), and CH_3NH_2 and C_6H_6 (employing a double-ζ basis), the wave functions were obtained by geometry optimization using a versatile *ab initio* package MICROMOL [15]. The topography of $\gamma(\mathbf{p})$ was analyzed by isolating its critical points (CP's), i.e., the points in momentum space at which $\nabla_{\mathbf{p}}\gamma(p_x,p_y,p_z)=\mathbf{0}$. For Gaussian-type functions used herein, one readily obtains analytical expressions for the first and second derivatives of $\gamma(\mathbf{p})$. The second derivatives at CP form the elements of the Hessian matrix H, given by $H_{ij}=\partial^2\gamma(\mathbf{p})/\partial p_i\partial p_j$. The Hessian, upon diagonalization, gives the eigenvalues $\lambda_1,\lambda_2,\lambda_3$, which essentially are the curvatures of the EMD at the critical point. To further contrast between bonding and nonbonding cases, a similar study was carried out on the EMD for the aforementioned molecular systems in the separated-atom premise, i.e., with the constituent atoms in molecular nuclear configuration, but with their atomic wave functions described using comparable basis sets, frozen.

As has been pointed out in a previous study [4], the origin is *always* a critical point in the topology of the molecular EMD, a result which stems from the fact that the molecular EMD has to be inversion symmetric about the point $\mathbf{p}=0$, thus forcing it to be a critical point. The point $\mathbf{p}=\mathbf{0}$ also qualifies to be the "point" in the point group of the EMD [4], since all symmetry operations in $\mathbf{p}$ space leave it invariant.

For convenience, the molecules studied herein may be classified as (a) diatomic and linear molecules, (b) isoelectronic molecules, and (c) cyclic systems of hydrocarbons and with one or more heteroatoms. The topography of these classes will be discussed below.

A. Diatomic and linear molecules

This class of molecular $\gamma(\mathbf{p})$ has been extensively studied in the literature: The guiding principles mentioned in Sec. I are mainly extracted from the study of diatomic molecules. We subdivide this class of molecules into two types, viz., molecules formed from atoms with exclusively s-type orbitals, viz., H, He, Li, and Be, and molecules formed from atoms with *both* s- and p-type of orbitals.

The molecules H_2, LiH, and Li_2 fall into the first category. Coulson [2] first showed that $\gamma(\mathbf{p})$ for H_2 has a maximum at $\mathbf{p}=\mathbf{0}$. We observe that a similar behavior is evinced by *all* the molecules that have exclusively s-type orbitals at their atomic level. Except for this unique global maximum [i.e., a unique $(3,-3)$ type of CP at $\mathbf{p}=\mathbf{0}$], $\gamma(\mathbf{p})$ for a molecule in this class is deprived of any other type of CP in its topology. That $\mathbf{p}=\mathbf{0}$ is a maximum is evident from the expression for s-type contributions to molecular $\gamma(\mathbf{p})$ for Gaussian orbitals:

$$\gamma(\mathbf{p})=\sum_{\mu,\nu} P_{\mu\nu} e^{-p^2/[4(\alpha_\mu+\beta_\nu)]}\cos(\mathbf{p}\cdot\mathbf{R}_{AB}) \;, \qquad (2)$$

where $P_{\mu\nu}$ is charge-density bond-order matrix, α_μ and β_ν are primitive Gaussian exponents, and $\mathbf{R}_{AB}$ is the separation between atoms A and B. Evidently, $\gamma(\mathbf{0})$ will turn out to be maximal owing to the presence of the cosine term. This significant maximal s contribution to $\gamma(\mathbf{p})$ also suggests that such a feature is not an artifact of any peculiar basis set and will be retained even after inclusion of polarization terms. This conjecture has been confirmed by employing double-ζ polarized (DZP) basis sets for the above molecular systems.

For the other category of molecules, involving both s *and* p orbitals at their atomic level, a $(3,-1)$ type of CP is *never* found to occur at $\mathbf{p}=\mathbf{0}$. All the other types of CP's of rank 3 are exhibited at $\mathbf{p}=\mathbf{0}$ for different molecular systems: A strict $(3,+3)$ minimum is observed for N_3^-, OH^-, HF, and LiF molecules [for these molecules a pair $(3,-3)$ or $(3,+1)$ type of CP is always found along the "bonding" direction, viz., the p_z direction], a $(3,+1)$ saddle for N_2, HCN, C_2H_2, and CN^-, and a $(3,-3)$ maximum for the CO and BF molecules (cf. Table I).

A CP is said to be degenerate when a rank of the CP is less than the dimensions of space; i.e., at least one of the eigenvalues of the Hessian is zero. According to catastrophe theory [16], a strictly isolated degenerate CP results from the coalescence of two or more nondegenerate CP's at a point. From the studies of the $\mathbf{r}$-space electron density $\rho(\mathbf{r})$, this coalescence gives rise to instability in the molecular structure: Any *other* nuclear configuration in the neighborhood of the unstable molecular structure associated with the degenerate CP is stable. The analysis of degenerate CP's essentially subscribes to catastrophe-theoretical analysis, which exhaustively classifies these instabilities. Another case that may occur is that a function is extremal along a line or a curve, leading to a curve of degenerate CP's. Such a type of behavior is also seen to occur in the case of another (albeit unrelated) scalar field of chemical interest, viz., the molecular electrostatic potential [17].

The critical-point analysis of diatomic and linear molecules is of special interest since $\gamma(\mathbf{p})$ for all these molecules necessarily have a $D_{\infty h}$ symmetry. Thus any CP lying off the molecular axis forms a continuous ring of nonisolated degenerate CP's of rank 2, a fact which entails that the direction of degeneracy (i.e., the direction i such that $\lambda_i=0$) does not remain fixed. A three-dimensional grid plot of a plane containing a degenerate ring of CP's for a fixed $p_z=0$ for C_2H_2 molecules is displayed in Fig. 1, which resembles an inverted pig trough with a curve of maxima satisfying the equation of a circle. The critical mountain of degenerate CP's in the present case can be broken up into ripples of continuously connected nondegenerate maxima and saddles. The form of the function depicted in the Fig. 1 resembles the function

$$F(p_x,p_y)=\alpha(p_x^2+p_y^2)-(p_x^2+p_y^2)^2 \;.$$

Hence a cut in the p_x-p_y plane passing through the origin resembles the function $f(x)=\alpha x^2-x^4$. As it turns out, the nonisolated degenerate ring of CP's in this case is indeterminate and has infinite codimensions [16–18].

The degenerate CP's in this example are, of course, stable; i.e., if the geometry of the molecule is slightly perturbed, the ring of degenerate maxima is still retained. This property is in contradistinction with the other *isolated* degenerate CP's found for some peculiar molecular structures [12] in the topology of $\rho(\mathbf{r})$, wherein a slight perturbation in the geometry leads to the nonexistence of degenerate CP's [12]. This feature may be manifested in

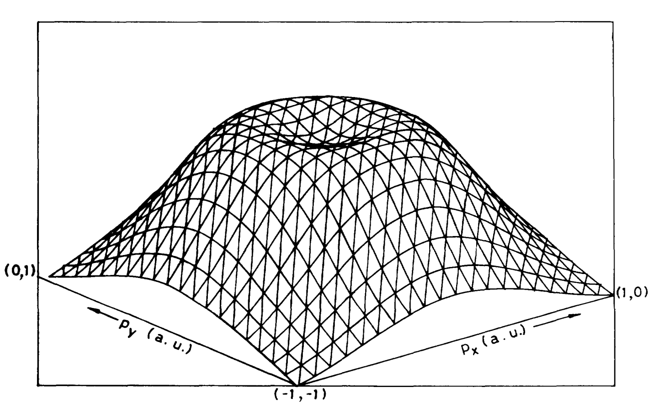

FIG. 1. Grid plot of $\gamma(\mathbf{p})$ for the C_2H_2 molecule in the p_x-p_y plane displaying a ring of nonisolated degenerate critical points (see Sec. II for details). All values are in atomic units.

the inherent instability of *isolated* degenerate CP's. The nonisolated degenerate CP's found here in the $\gamma(\mathbf{p})$ topology are indeed stable and are a consequence of $D_{\infty h}$ symmetry of linear molecules in **p** space. Although this occurrence of a ring of degenerate CP's is a simple consequence of symmetry, this unusual feature is not found in its **r**-space counterpart $\rho(\mathbf{r})$, in its ground state, and such an existence is particular to and hence is of special interest in **p** space.

B. Isoelectronic molecules

Four isoelectronic series with 10, 14, 18, and 24 electrons, respectively, were investigated in the present study: (1) CH_4, NH_3, H_2O, HF, and OH^-, (2) N_2, CO, BF, HCN, and C_2H_2, (3) ethane (C_2H_6), methyl amine (CH_3NH_2), methanol (CH_3OH), and methyl fluoride (CH_3-F), and (4) cyclopropane (C_3H_6), ethylenimine (C_2H_5N), ethylene oxide (C_2H_4O), and diaziridine (CH_4N_2).

Molecules belonging to series (1) all exhibit, for their EMD, at $\mathbf{p}=0$, a strict minimum [CP of $(3,+3)$ type], while those within series (3) show a $(3,+1)$ saddle (cf. Table I). This behavior may be attributed to a similar type of molecular bonding within a given series. The occurrence of criticalities is also dictated by the symmetry of molecules in **p**-space [4]. For instance, by virtue of D_{2h} symmetry, H_2O is seen to have four $(3,+1)$ saddles symmetrically located (on the vertices of the parallelogram in p_y-p_z plane) and eight $(3,-1)$ CP's. For the second isoelectronic series, however, the above trend at $\mathbf{p}=0$ is not observed (cf. Table I), which may be traced back to the differences in the nature of the bonding, according to whether it is covalent or ionic. Partial-wave analysis studies [19] also support the above observation in the sense that the $\gamma(\mathbf{p})$'s for CO and BF exhibit marked similarity as compared with that for N_2.

Epstein [20] and Hirst and Liebmann [21] have studied the radial momentum density $I(p)$ [where $I(p) = (4\pi)^{-1}\int \gamma(\mathbf{p})d\Omega_{\hat{p}}$] for 10 and 18 electron molecular systems, respectively. As the polarity of substituents increases from CH_4 to HF [as in series (1) above] and from C_2H_6 to CH_3F [in series (3)], the maximum value of $I(p)$, viz., $I_{\max}$ occurring at $p=p_{\max}$, decreases, accompanied by an increase in the $p_{\max}$ value. A similar trend is ap-

TABLE I. Table of curvatures (eigenvalues) of critical points at $\mathbf{p}=0$ and types of some critical points found away from $\mathbf{p}=0$ in the topography of molecules (all values in a.u.).

Molecule	λ_1	λ_2	λ_3	Types of CP's away from $\mathbf{p}=0$
H_2	−4.559	−4.559	−5.558	
CO	−2.733	−2.733	−4.659	
C_3H_6	−10.76	−10.76	−0.824	
Li_2	−626.6	−626.3	−825.5	
LiH	−91.82	−91.82	−60.42	
BF	−17.72	−17.72	−14.99	
C_2H_4	−17.44	−23.29	−39.72	
C_2H_5N	−11.70	−1.181	−10.81	
C_6H_6	−1.970	−1.970	20.70	$(3,-3)$
C_4H_6	−10.97	−4.509	11.90	$(3,-3)$
CH_4N_2	−7.514	0.910	−5.494	$(3,-3)$
C_2H_4O	−7.610	0.317	−8.562	$(3,-3)$
CH_3OH	2.445	2.920	−7.072	$(3,-1)$, $(3,-3)$
CH_3F	2.426	2.426	−5.565	$(3,-1)$, $(3,-3)$
CH_3NH_2	3.315	2.732	−7.759	$(3,-1)$, $(3,-3)$
C_2H_6	3.126	3.126	−12.49	$(3,-1)$, $(3,-3)$
C_2H_2	7.174	7.174	−4.405	degenerate CP's
HCN	3.495	3.509	−2.265	degenerate CP's
N_2	1.099	1.099	−3.372	degenerate CP's
HCHO	0.972	1.464	−4.470	$(3,-1)$, $(3,-3)$
N_2H_4	−8.572	2.757	2.804	$(3,-1)$ $(3,-3)$
BH_3	1.341	−11.37	1.341	$(3,-3)$
CN^-	0.038	0.038	−4.443	
LiF	5.047	5.047	16.11	degenerate CP's, $(3,-3)$
HF	0.867	0.867	1.326	degenerate CP's, $(3,-3)$
CH_4	4.028	4.028	4.028	$(3,-1)$, $(3,-3)$
NH_3	3.349	3.349	4.140	$(3,+1)$, $(3,-1)$, $(3,-3)$
H_2O	1.933	2.554	2.225	$(3,+1)$, $(3,-1)$, $(3,-3)$
OH^-	2.834	0.564	0.564	degenerate CP's, $(3,-3)$
N_3^-	0.043	0.690	0.690	degenerate CP's, $(3,+1)$

TABLE II. Momentum densities and average momentum $|\mathbf{p}_{\max}|$ (in a.u.) at $(3,-3)$ CP's (maxima) in $\gamma(\mathbf{p})$ for molecules of the isoelectronic series with bond polarities (κ) of molecules.[a]

Molecule	$\gamma(\mathbf{p})$	$\lvert\mathbf{p}_{\max}\rvert$	$\kappa=1-\dfrac{\lambda_L}{\lambda_H}$
	10-electron series		
CH_4	1.467	0.357	0.000
NH_3	1.026	0.467	0.191
OH^-	0.747	0.481	0.801
H_2O	0.663	0.512	0.250
HF	0.434	0.565	0.347
	18-electron series		
C_2H_6	2.447	0.263	0.000
CH_3NH_2	1.956	0.317	0.176
CH_3OH	1.719	0.320	0.163
CH_3F	1.515	0.308	0.000
	24-electron series		
C_3H_6	2.996	0.000	0.000
C_2H_5N	2.633	0.000	0.076
C_2H_4O	2.358	0.096	0.112
CH_4N_2	2.123	0.175	0.269

[a]See text of Sec. II for the definition of bond polarity of each isoelectronic series.

parent from Table II for the momentum density by examining its global maxima, i.e., $(3,-3)$ type of CP's in the $\gamma(\mathbf{p})$ topology. From Table II it is clear that the momentum density decreases with an increase in the electronegativity of an atom or a group attached to a given fixed atom or a group, whereas the $p_{\max}$ value increases. In polar molecules this spread of the momentum distribution with increasing electronegativity of the substituent atom or group may be ascribed to a complementary behavior in coordinate space, viz., a biased charge distribution of $\rho(\mathbf{r})$, the electron density. However, the 14-electron series does not exhibit the above feature because of different types of bonding in this series. As has been pointed out by Koga, Nakao, and Hao [6], bond polarity can be related to anisotropies in the molecular kinetic energy. A correlation of the curvatures of the CP at $\mathbf{p}=0$ is observed with the bond polarity or distribution polarity, depending on whether the system under study is diatomic or polyatomic. To bring out explicitly this correlation for the 10- and 18-electron series that have, respectively, $(3,+3)$ and $(3,+1)$ type CP at $\mathbf{p}=0$, the ratio of curvatures of two higher positive-valued eigenvalues may be considered, whereas for the 24-electron series, the ratio of two negative-valued eigenvalues may be taken into account. As a measure of the distribution polarity, a numerical index κ is set up which compares different bond polarities on equal footing: $\kappa=1-\lambda_L/\lambda_H$, with $|\lambda_L|\leq|\lambda_H|$. The 10- and 24-electron series, as evidenced by an increase in κ, show a good correlation between this distribution polarity index and increase in electronegativity of the atom or group (cf. Table II). Such a property, however, is not found to hold for the 18-electron series.

C. Ring systems

The study of ring systems of hydrocarbons, viz., cyclopropane and benzene, showed varied topographical structures. In the case of cyclopropane the existence of a unique $(3,-3)$ maximum at $\mathbf{p}=0$ is discernible in its $\gamma(\mathbf{p})$ topology. In the cyclopropane ring, when one of the —CH_2 groups is replaced by a —NH group, leading to the ethylenimine molecule, this maximal $\gamma(\mathbf{0})$ character persists without any extra CP's creeping in. However, when —CH_2 is replaced by an —O group to form ethylene oxide, a $(3,-1)$ CP occurs at $\mathbf{p}=0$ along with a pair of $(3,-3)$ kinds of CP's perpendicular to the C—C—O ring plane. Similarly, if two —NH groups replace the two —CH_2 groups to form a diaziridine molecule, a $(3,-1)$ saddle occurs at $\mathbf{p}=0$ and two local maxima, i.e., a pair of $(3,-3)$ CP's, are observed perpendicular to the C—N—N plane. Similar characteristics are also exhibited by benzene with a $(3,-1)$ saddle at $\mathbf{p}=0$ and a pair of maxima perpendicular to the plane of the molecules. This occurrence of the $\gamma(\mathbf{p})$ maximum off the plane may be viewed as yet further supportive evidence for the generalized bond-directionality principle [10].

The topographical analysis for some of the molecules in the present study has been carried out with a STO-3G (minimal) basis and 6-31G* or DZP basis. It was observed that a minimal basis set is insufficient to study the critical structure of molecules. However, from studies of polarized basis sets, it is clear that the DZ basis set used in the present study exhibits the correct critical structure in the sense that it leads to qualitatively identical topographies.

The topographical study of the corresponding separated-atom (SA) cases for all the molecules studied herein reveals that $\mathbf{p}=0$ is always a critical point; however, the nature of this CP in general changes as atoms bind to form the molecule. Another general observation from the topography of $\gamma_{\mathrm{SA}}(\mathbf{p})$ is that exclusively $(3,-3)$ type of CP's, i.e., maxima, are seen to occur *away* from the origin. A $(3,+3)$ CP, i.e., a minimum, is *never* found in the topology of $\gamma_{\mathrm{SA}}(\mathbf{p})$, suggesting that the occurrence of a minimum in the molecular $\gamma(\mathbf{p})$ is a relaxation effect brought about by molecular-bond formation. The nature of CP's at $\mathbf{p}=0$ for $\gamma_{\mathrm{SA}}(\mathbf{p})$ of the H+H system is a maximum, since the atomic $\gamma(|\mathbf{p}|)$ for hydrogen is monotonic in $|\mathbf{p}|$. The H+F system also displays a maximum at $\mathbf{p}=0$ because of the predominance of monotonic behavior of $\gamma(|\mathbf{p}|)$ for hydrogen over the nonmonotonic behavior of $\gamma(|\mathbf{p}|)$ for fluorine. In a similar fashion, the nature of CP's at $\mathbf{p}=0$ for polyatomic molecules in the separated-atom premise may be analyzed, to seek any trend in the deviations in the $\gamma(\mathbf{p})$ topography, characterizing the process of bond formation.

From the above observations, one may infer that the occurrence of CP's at other positions than the origin and also of types other than the maximum in the topology of the molecular EMD are also indicative of bonding. In the case of some linear molecules, as noted before, a ring of degenerate CP's is observed around the p_z axis; the absence of such a feature in $\gamma_{\mathrm{SA}}(\mathbf{p})$ implies that this critical degenerate ring formation may be taken to be a signature of bonding.

III. ANISOTROPIES IN MOMENTUM DENSITY: A TOPOGRAPHICAL VIEW

The analysis of topology momentum density is somewhat obscured because of the lack of a nuclear configuration unlike for its $\rho(\mathbf{r})$ counterpart. As mentioned earlier, the origin $\mathbf{p}=\mathbf{0}$ is *always* a critical point and all possible types of criticalities are observed at this point for different molecular structures. Also, the type of CP found at $\mathbf{p}=\mathbf{0}$ is never found anywhere else in the topology of the molecule. The most interesting observation is that of a hierarchy of CP's (cf. Table I): Whenever a minimum, i.e., a $(3,+3)$ type CP, occurs at $\mathbf{p}=\mathbf{0}$, all *other* types of CP's, viz., $(3,+1)$, $(3,-1)$, and $(3,-3)$, are seen to occur at some isolated points away from the origin. Further, if a $(3,+1)$ nature at $\mathbf{p}=\mathbf{0}$ is exhibited, only $(3,-1)$ nd $(3,-3)$ types of CP's are seen to arise elsewhere. Moreover, when a $(3,-1)$ type of CP exists at the origin, it could be accompanied by exclusively $(3,-3)$ type of CP's at some $\mathbf{p}\neq\mathbf{0}$ in the $\gamma(\mathbf{p})$ topology. Finally, a strict local maximum, i.e., a $(3,-3)$ type of CP at $\mathbf{p}=\mathbf{0}$, demands that it is a unique critical point and $\gamma(\mathbf{p})$ is deprived of any other CP's in its topology. Thus a minimum in $\gamma(\mathbf{p})$, if it exists, could only be observed at $\mathbf{p}=\mathbf{0}$ as inferred from the molecular systems studied here.

Yet another noteworthy feature in the topology of $\gamma(\mathbf{p})$, barring the cases which have a maximum at $\gamma(\mathbf{0})$ (which is a unique CP in that case), is the occurrence of directional maxima: Proceeding from the origin $\mathbf{p}=\mathbf{0}$ outward, it is seen that a strict maximum in $\gamma(\mathbf{p})$ always lies the *farthest* with other possible intermediate criticalities in between. After attainment of the said strict maximum, $\gamma(\mathbf{p})$ decreases monotonically, to vanish asymptotically. That a maximum [rather than any other type of CP, viz., $(3,+1)$ or $(3,-1)$] which always occurs at higher $|\mathbf{p}|$ values may, albeit heuristically, be explained as follows: During bond formation at equilibrium distance, the kinetic energy of the given molecule increases, particularly in the internuclear region. From the connection of $\gamma(\mathbf{p})$ and kinetic energy [the kinetic energy is equal to $\int\gamma(\mathbf{p})(p^2/2)d^3p$], one can say that higher kinetic energy implies a substantial contribution from higher-momentum values, but for a finite system, $\gamma(\mathbf{p})$ itself diminishes at higher momenta. Hence there is a break-even point at a sufficiently large momentum value around which the probability density $\gamma(\mathbf{p})$ is maximal.

The analysis of CP's at $\mathbf{p}=\mathbf{0}$ may also be used to identify the EMD anisotropies, i.e., preferential momentum directions along which such a preponderant $\gamma(\mathbf{p})$ is seen. This may be analyzed as follows: Consider the eigenvalues of the Hessian corresponding to the CP at $\mathbf{p}=\mathbf{0}$; a negative curvature along a direction in $\mathbf{p}$ space implies that in the neighborhood the momentum density will decrease radially outward, whereas a positive curvature indicates an increase. Thus it is expected that a maximum in the momentum density may occur along such a direction where the positive curvature associated with the CP at $\mathbf{p}=\mathbf{0}$ is itself maximal. This trend has indeed been observed for all the molecular $\gamma(\mathbf{p})$'s studied here, except for those cases with a unique maximum at $\mathbf{p}=\mathbf{0}$. Consider, now, a polyatomic molecule having a minimum, i.e., a $(3,+3)$ type CP (all three eigenvalues positive) at $\mathbf{p}=\mathbf{0}$; a maximum in $\gamma(\mathbf{p})$ is observed along the direction in which the positive curvature is maximum. The direction along which the next lower (intermediate) valued curvature encounters has a $(3,-1)$ type of CP and that associated with the lowest one has a $(3,+1)$ type of CP. This is demonstrated with the example of the water molecule, which has, for its criticality at $\mathbf{p}=\mathbf{0}$, all three eigenvalues positive (cf. Table III). One of the most interesting cases is posed by methane, which has all *equal* positive eigenvalues for the Hessian at $\mathbf{p}=\mathbf{0}$, (if 2 eigenvalues, i.e., the curvatures, are equal or almost equal, then both the corresponding momentum directions exhibit CP's), shows 6 maxima in $\gamma(\mathbf{p})$, a pair each along p_x,p_y,p_z axes, 12 $(3,-1)$ CP's, 1 in all quadrants of the momentum-coordinate planes,and 8 $(3,-1)$ CP's located at the 8 vertices of a cube, by virtue of O_h symmetry. For a molecule having a $(3,+1)$ type of CP at $\mathbf{p}=\mathbf{0}$, a $(3,-3)$ maximum as well as a $(3,-1)$ saddle are found along the directions according to the magnitudes of positive curvatures, as illustrated in Table III for the CH_3OH molecule. In this case, λ_2 is maximal positive; hence a pair of local maxima would be seen along the corresponding direction. For a $(3,-1)$ CP at $\mathbf{p}=\mathbf{0}$, the direction in which the only

TABLE III. Anisotropies in momentum density for representative molecules of $(3,+3)$, $(3,+1)$, and $(3,-1)$ type critical points at $\mathbf{p}=\mathbf{0}$ (all values in a.u.).

	Eigenvalues of CP's at $\mathbf{p}=\mathbf{0}$			Momentum coordinates of other CP's in molecules				Type of critical
Molecule	λ_1	λ_2	λ_3	p_x	p_y	p_z	$\gamma(\mathbf{p})$	point
H_2O	1.933	2.554	2.225	0.0	0.0	±0.535	0.658	$(3,-3)$
				0.0	±0.512	0.0	0.663	$(3,-3)$
				(±)0.110[a]	(±)0.293[a]	(±)0.411[a]	0.654	$(3,-1)$
				±0.526	0.0	0.0	0.638	$(3,+1)$
				0.0	±0.308	±0.412	0.654	$(3,+1)$
CH_3OH	2.445	2.920	−7.072	0.0	(±)0.320[a]	(±)0.001[a]	1.719	$(3,-3)$
				±0.301	0.0	0.0	1.703	$(3,-1)$
C_4H_6	−10.97	−4.509	11.90	0.0	0.0	±0.337	3.888	$(3,-3)$

[a] (±)indicates that only the upper and only lower signs are considered for two points generated for all three p_x, p_y, and p_z.

positive curvature lies is seen to be the preferred momentum direction, as is demonstrated in Table III for the *trans-* butadiene molecule. Since for the molecules having $(3,-3)$ maximum at $\mathbf{p}=\mathbf{0}$, no other type of CP is seen to exist, similar definitive arguments regarding the anisotropies are not possible. However, one can say that the higher the negative curvature, the higher is the falloff in the momentum density in that particular (momentum) direction. Thus anisotropies in the momentum density of polyatomic molecules are clearly related to the criticality of $\gamma(\mathbf{p})$ at $\mathbf{p}=\mathbf{0}$. The above arguments are evidently valid for a host of diatomic molecules also, since some of these show a ring of CP's, whereby it can be concluded that any direction apart from the p_z direction is preferred by the momenta.

A similar analysis applied to the separated-atom case reveals that there is *no preferential direction* of momenta in $\gamma_{\mathrm{SA}}(\mathbf{p})$ in that all CP's are seen to occur at $(p_x=\pm p_0, p_y=\pm p_0, p_z=\pm p_0)$. As remarked above, the very existence of anisotropies evinced by preferential momentum directions can be looked upon as a consequence solely of bond formation.

IV. CONCLUDING REMARKS

An attempt has been made here to view the impact of molecular-bond formation on the critical structure of the electron-momentum density of diatomic as well as polyatomic molecular systems. The salient deviations of the critical-point structure, characteristic of bond formation, become obvious upon a comparison with the corresponding separated- (unbonded) atom cases. Interestingly enough, some linear molecules are seen to possess a ring of degenerate CP's, as is demanded by the $D_{\infty h}$ symmetry for $\gamma(\mathbf{p})$. The radial momentum density $I(p)$, as well as $\gamma(\mathbf{p})$, shows similar trends in terms of shifting its maxima outward with increasingly electronegative group substitution. A fair correlation of ratios of curvatures of a CP at $\mathbf{p}=\mathbf{0}$ with the distribution polarity for some isoelectronic species is observed. Thus, in general, one can say that information such as the geometry of a molecule, type of bonding, or effects of different types of bonding will have a direct bearing on the criticality at $\mathbf{p}=\mathbf{0}$. This follows from the $\mathbf{r}$-space valence-orbital contribution to the electron density being mapped in $\mathbf{p}$ space to lower values of momentum, as a result of a complementary reciprocity in $\mathbf{r}$ and $\mathbf{p}$ spaces brought about by the Fourier-transform connection between the respective wave functions.

The present study also addresses directly the anisotropies in the molecular EMD via the topographical analysis as against their extraction by indirect means reported in earlier studies in this direction [5–10]. The preferential direction of momenta leading to anisotropies in the EMD dictated by the preponderance of the EMD can be associated with the curvatures (eigenvalues) of the Hessian matrix corresponding to the criticality at the origin. It is hoped that the present study will impart an impetus for further studies such as reactions in momentum space via topographical analyses of the molecular EMD, which are currently being carried out in our laboratory.

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[18] For convenience, let us define a k jet first: For any smooth function $f(x)$, the Taylor series at the origin is defined as $f(x)=\sum_{r=0}^{\infty}(1/r!)(\partial^r f/\partial x^r)|_0 x^r$. Truncation of the series at degree k gives a k jet $j^k f(x) =\sum_{r=0}^{k}(1/r!)(\partial^r f/\partial x^r)|_0 x^r$. A function f is said to be k determined if the k jet of f is such that any function $f+g$ (where g is of order $k+1$) is locally equivalent by a smooth coordinate change to a k jet of f, i.e., $j^k(f+g)\sim j^k f$. A function is finitely determined if it is k determined for some finite k; if f has no such finite k, then it is called indeterminate, e.g., $f(x,y)=x^2y$. The codimension of a function is the minimum number of parameters required to describe completely the topological possibilities generated by small perturbations in a function.

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