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Qualitative Characterization of the P−C Bonds in Ylides of Phosphorus

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The aim of this paper is qualitative understanding of the behavior of electrons in the ylides of phosphorus by means of the sharing amplitudes and the volume−point sharing indices (Fulton, R. L. *J. Phys. Chem.* **1993**, *97*, 7516). This paper supplements a previously carried out quantitative analysis (Mitrasinovic, P. M. *J. Comput. Chem.* **2001**, *22*, 1387−1395) of the P−C bonds in the ylides of phosphorus that was based solely on the sharing indices. The sharing amplitude and the sharing indices are quantitative measures of the degree to which an electron, as a wave, is shared between two spatial points in a many electron system. As a quantitative measure of the degree of sharing of an electron between two disjoint regions, the delocalization index (Fulton, R. L. *J. Phys. Chem.* **1993**, *97*, 7516) is used to display the shell structure in phosphorus. The delocalization shell structure displays spatial regions from which electrons are greatly delocalized as well as regions in which electrons are essentially localized. By varying the positions of the fixed points in the valence region of the phosphorus, the sharing amplitudes exhibit a more diffuse character on the phosphorus and are tightly placed on the carbon in the complexes PH_3CH_2 and $PHCH_2$. Since the nodes formed in the sharing amplitudes appear only as remnants of nodes in the volume−point sharing indices, the circular shape of the minimum of the volume−point sharing index from the carbon atom in the vicinity of the phosphorus in PH_3CH_2, having the radius of about 1.7 au (within the valence shell of the phosphorus), indicates a remnant of a 3s or a 3p contribution. For the positions of the fixed points along the P−C bonds, the shapes of the nodal lines of the sharing amplitudes indicate an increase of the 2p character on the carbon in PH_3CH_2 in comparison to that in $PHCH_2$. The increase of 2p character on the carbon in PH_3CH_2 is in agreement with the values of the P−C interbasin sharing indices of 0.92 and 1.30 for PH_3CH_2 and $PHCH_2$, respectively. The values of 0.87 and 1.54 correspond to a classical C−C single bond and a classical C═C double bond (Mitrasinovic, P. M. *J. Comput. Chem*. **2001**, *22*, 1387−1395) (see Tables 1−3 given below). The volume−point sharing index from the carbon atom, which describes the sharing emanating from a basin microscopically, shows the delocalization of an electron over the carbon, phosphorus and hydrogen (bonded to the phosphorus) basins in $PHCH_2$ and PH_3CH_2. This delocalization was reflected in ref 2 by the values of 0.13 and 0.17 for the sharing indices between the carbons and hydrogens on phosphorus in PH_3CH_2 and $PHCH_2$, respectively. This substantial delocalization of an electron over the carbon, phosphorus and hydrogen basins in PH_3CH_2 and $PHCH_2$ indicates the special stabilization of the carbanion. The electron density does not mimic the volume−point sharing index from the carbon basin in PH_3CH_2. The volume−point sharing index from the phosphorus basin resembles the electron density in PH_3CH_2 within the core of the phosphorus basin. The volume−point sharing index from the carbon basin in $PHCH_2$ displays a shape very similar to that in PH_3CH_2 qualitatively, especially in terms of the electron delocalization over the C, P, and H (attached to the phosphorus) basins. The clear distinction to the volume−point sharing index in PH_3CH_2 is much broader peak at the primary carbon basin, as quantitatively expressed in Mitrasinovic, P. M. *J. Comput. Chem*. **2001**, *22*, 1387−1395 by the values of the P−C interbasin sharing indices for $PHCH_2$ and PH_3CH_2 which are given above. This article accompanied by Mitrasinovic, P. M. *J. Comput. Chem*. **2001**, *22*, 1387−1395 puts our understanding of the electron behavior in phospho-ylides at a more rigorous basis.

I. Introduction

Many unusual physical and chemical properties of ylides have been accounted for by means of the d orbitals.[3,4] Some properties, such as the P−C bond length in PH_3CH_2,[5] can be predicted to a satisfactory extent only if d orbitals are taken into account by the quantum mechanical calculations. Some calculations involving *n*-electron treatment indicate the mixing of the delocalized lone pair with the P−C σ-bond.[6] It results in the formation of two highly polarized τ bonds that are not the same. The role of d orbitals on the phosphorus is supported by the molecular orbital pictures with respect to PH_3CH_2.[7] The localization procedure[8] of molecular orbitals used in ref 7 is not unique. These molecular orbitals are in accordance with the investigations both of Kutzelnigg[9] and of Gordon et al.[10] General valence bond (GVB) treatment of the bonding structure in simple ylides by D. A. Dixon et al.[11] shows two the P−C τ bond (bent) pairs that are not equivalent, but similar to those obtained by Lischka (ref 7). The authors of ref 11 stated on page 7016: "the GVB orbitals are obtained by a rigorous energetic localization technique." On the basis of the role of d orbitals, an explicit

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TABLE 1: Bond Indices for Some Simple Molecules[25]

molecule	bond	HF/ 6-31++G**	MP2/ 6-31++G**
$H_aH_bH_cC_aC_bH_dH_eH_f$	C_a-H_a	0.961	0.852
	C_a-C_b	0.984	*0.868*
	H_a-H_b	0.046	0.038
	H_a-C_b	0.045	0.037
	H_a-H_d	0.004	0.004
	H_a-H_f (trans)	0.012	0.011
$H_aH_bC_aC_aH_cH_d$	C_a-H_a	0.982	0.872
	C_a-C_b	1.876	*1.545*
	H_a-H_b	0.042	0.033
	C_a-H_c	0.067	0.052
	H_a-H_c(cis)	0.007	0.006
	H_a-H_d (trans)	0.015	0.012

TABLE 2: PH_3CH_2: The Total Interbasin Sharing Indices[2]

basin	C	P	H(C)	H(C)	H(P)	H(P)	H(P)
C	11.22						
P	0.92	21.28					
H(C)	0.92	0.03	0.98				
H(C)	0.92	0.03	0.03	0.98			
H(P)	0.13	0.58	0.01	0.01	2.30		
H(P)	0.12	0.61	0.01	0.01	0.10	2.25	
H(P)	0.12	0.61	0.01	0.01	0.10	0.09	2.25

classification of the phospho-ylides can be found on page 40 of ref 3: "...the phosphonium ylide clearly should not be classified as a hypervalent molecule as its bonding can easily be described by simple chemical principles." In contrast to this prediction, the author of an important review on the bonding in phosphines, phosphine oxides, and phosphonium ylides suggests in the title: "no *d* orbitals but...".[12] It is also pointed out on page 1370 of ref 12: "an ylide is a hypervalent molecule in which a three-center bond is reduced to a two-center bond using...". Two types of hypervalent binding environments described by Musher[13] are very important concepts for compounds such as $R_3PCR'_2$.[14−20] The formation of 3c−4e bonding causes that the stabilizing effect is due to the presence of 4 electrons on three centers. Nyuláaszi, Veszprémi, and Réffy[21] have discussed the similar strengths and lengths of λ^3 and λ^5, the P−C bonds, on the basis of the formation of a three-center four-electron (3c−4e) bonding structure. The authors have also discussed the extent of multiple bonding in CH_2PH_3 and established that the P−C bond should be a double bond rather than an ylidic bond. The conclusion is based on the topological features of the charge density, the strengths of the P−C bonds, and the Mulliken charges on the carbon and phosphorus atoms in $PHCH_2$ and PH_3CH_2 (in line with the ylene form). However, Musher[13] omitted to consider charge separated structures and did not account for hybridization between s and p orbitals. Recently reported results[22] dealing with PH_3CH_2 and $P(CH_3)_3CH_2$, based on the NBO analysis of the molecules, show that there is little or no double bond character in the P−C bond in the ylides.

A detailed quantitative characterization of the carbon−phosphorus bond in trivalent and pentavalent carbon phosphorus molecules $PHCH_2$, PH_3CH_2, PF_3CH_2, and PH_3CHF, based solely on the sharing indices, resolved a controversy related to the nature of the P−C bonds.[2] Fluorinated derivatives indicated substituent induced effects concerning the extent of multiple bonding. Four aspects of the analysis were dominant. The electronic charge considerations showed that the ylides could be observed to be of the form (− + −) with respect to the basin charges of the carbon, phosphorus, and hydrogen or fluorine (on phosphorus) atoms (Table 4). The carbon−phosphorus interbasin sharing indices indicated that the P−C bonds are: (mostly) double in $PHCH_2$ (Table 3), and single in PH_3CH_2 (Table 2), PF_3CH_2, and PH_3CHF. On the basis of the group basin charges and inter-group sharing indices between the CH_2 (or CHF) groups and the $PH_{1,3}$ (or PF_3) groups, the molecules are ionic with double bonds between the groups. The sharing indices between the carbon and atoms bonded to the phosphorus indicated that the electrons are delocalized over the basins of the following groups: CPH in $PHCH_2$, CPH_3 in PH_3CH_2, CPF_3 in PF_3CH_2, and CPH_3 in PH_3CHF. In the discussion of ref 2, it was pointed out that a further dissection of sharing of an electron in these compounds can be obtained by the sharing amplitudes and the volume−point sharing indices.

TABLE 3: $PHCH_2$: The Total Interbasin Sharing Indices[2]

basin	C	P	H(C)	H(C)	H(P)
C	10.53				
P	1.30	24.98			
H(C)	0.89	0.05	0.96		
H(C)	0.89	0.04	0.03	0.97	
H(P)	0.17	0.79	0.01	0.01	2.18

TABLE 4: Average Number of Electrons in Basins[2]

	basin						
molecule	C	P	H(C)	H(C)	H(P)	H(P)	H(P)
$PHCH_2$	6.90	13.58	0.98	0.98	1.58		
PH_3CH_2	7.17	12.03	0.99	0.99	1.62	1.60	1.60

The plan of this paper is as follows. The definitions of the sharing amplitude and the sharing indices[1] are given in part II. The primary intention of the part is to emphasize certain aspects of the concepts of sharing of an electron, which are directly related to considerations in following sections. Part III contains detailed qualitative descriptions of the sharing amplitudes with the fixed coordinates chosen in the valence region of the phosphorus in the molecules $PHCH_2$ and PH_3CH_2. This part clearly shows the beauties of the description of electron behavior developed by R. L. Fulton[1] that many contacts can be made with more traditional (and noninvariant) modes of interpreting electron behavior. The electron distribution of sharing of an electron in the complexes $PHCH_2$ and PH_3CH_2 is discussed in part IV by means of the volume−point sharing indices. The qualitative descriptions of the volume−point sharing indices are contrasted to those of the electron density.

II. Sharing Quantities

Let denote the space-spin coordinates by $\zeta \equiv (r\sigma)$ for each point. A Hermitian matrix $\boldsymbol{\rho}$, whose elements of the forms $\rho(\zeta;\zeta')$ are generally complex, can be diagonalized by a unitary transformation represented by a unitary matrix, **U**, constituting of the orthogonal eigenfunctions of $\boldsymbol{\rho}$, $\varphi_m(\zeta)$, and a diagonal matrix, $\boldsymbol{\Lambda}$, of real eigenvalues, ρ_m

$$\boldsymbol{\rho}(\zeta;\zeta') = \mathrm{U}_{\zeta}\boldsymbol{\Lambda}\mathrm{U}_{\zeta'}{}^{\pm}$$

with $\mathrm{Tr}\boldsymbol{\Lambda} = \sum_m \rho_m = 1$. $\boldsymbol{\rho}(\zeta;\zeta')$ can be expanded in terms of its orthonormal eignfunctions and eigenvalues as

$$\boldsymbol{\rho}(\zeta;\zeta') = \sum_m \varphi_m(\zeta)\rho_m\varphi_m^*(\zeta')$$

The new spin−orbitals $\varphi_m(\zeta)$ are called the natural orbitals. The numbers ρ_m are interpreted as occupation numbers of the natural orbitals.

The matrix $\boldsymbol{\rho}^{1/2}(\zeta;\zeta')$, which is the positive semidefinite square root of the single particle density matrix (normalized to 1), is conveniently found from the spectral representation of the density matrix,[23,24] as

$$\boldsymbol{\rho}^{1/2}(\zeta;\zeta') = \sum_m \varphi_m(\zeta)\rho_m{}^{1/2}\varphi_m^*(\zeta')$$

The matrix $\boldsymbol{\rho}^{1/2}(\zeta;\ \zeta')$ has the following property

$$\int d\zeta''\rho^{1/2}(\zeta;\zeta'')\rho^{1/2}(\zeta'';\zeta') = \rho(\zeta;\zeta')$$

The point−point sharing amplitude[1] $\langle\zeta;\zeta'\rangle$ is defined as

$$\langle\zeta;\zeta'\rangle = N^{1/2}\boldsymbol{\rho}^{1/2}(\zeta;\zeta')$$

The point−point sharing amplitude $\langle\zeta;\zeta'\rangle$ has a rich nodal structure reflecting the behavior of a single electron in a many electron system. In some respects the nodal structure is reminiscent of the nodal structure of orbitals, and orbitals sometimes mimic that structure.[25−27] The sharing amplitude $\langle\zeta;\zeta'\rangle$ has many of the characteristics of a transformation function together with a number of differences. The point−point sharing amplitude, being a function of (6 spatial + 2 spin) variables, is the closest one can get to a wave function for a single electron in a many electron system. The positions of the nodal surfaces are an invariant property of the amplitudes. The sharing amplitude displays the wavelike nature of an electron.

The point−point sharing index[1] is defined by

$$I(\zeta;\zeta') \equiv |\langle\zeta;\zeta'\rangle|^2$$

The point−point sharing index $I(\zeta;\zeta')$ is zero or positive. The physical interpretation of the point−point sharing index $I(\zeta;\zeta')$ is that $\mathrm{d}\zeta I(\zeta;\zeta')\mathrm{d}\zeta'$ is a measure of the degree to which a single electron is shared between a volume $\mathrm{d}\zeta$ about ζ and the volume $\mathrm{d}\zeta'$ about ζ'. It behaves very much like a probability.

It is also important to note the sum rules obeyed by this sharing index. The first sum rule is

$$\int \mathrm{d}\zeta'\ I(\zeta;\zeta') = N(\zeta)$$

where $N(\zeta)\mathrm{d}\zeta$ is the number of electrons in the volume $\mathrm{d}\zeta$ about ζ, and the second is

$$\int d\zeta N(\zeta) = N$$

The volume−point sharing indices give a quantitative measure of the degree of sharing of a single electron between the volume associated with an atom and a point. The definition of this index is

$$I_A(\zeta) \equiv \int_A \mathrm{d}\zeta'\ I(\zeta;\zeta')$$

the integral being over volume *A*. The quantity can be looked at as being the microscopic valence structure of an atom in a molecule. The nodes formed in the sharing amplitudes appear only as remnants of nodes in the volume−point sharing indices.

A subsequent integral of $I_A(\zeta)$ over volume *B* gives the volume−volume sharing index I_{AB}:

$$I_{AB} = \int_B \mathrm{d}\zeta\ I_A(\zeta)$$

The basin−basin sharing index, for $A \neq B$, represents a quantitative measure of how an electron, as a wave, is delocalized between the volumes associated with the atoms A and B. Note that the integration is over two disjoint volumes in space associated with the atoms A and B. This index is also called the delocalization index.

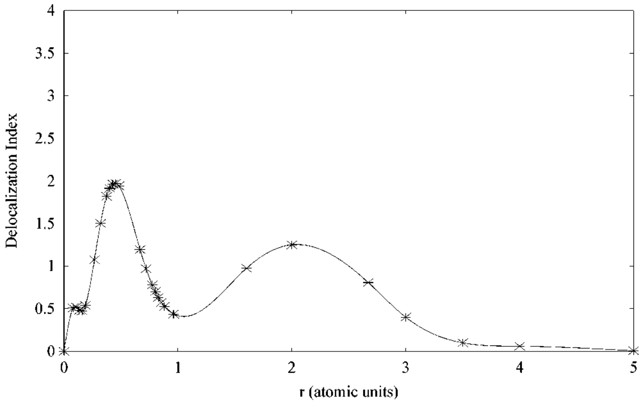

Figure 1. Delocalization index vs radius for P.

The sharing quantities are orbital independent, rooted in the single particle density matrix, and do not depend on arbitrary localization procedures.

III. Sharing Amplitudes

The fundamental idea underlying the concept of sharing of an electron in molecules is that an electron, as a generalized wave, is delocalized over all the atoms in a molecule. The point−point sharing amplitude $\langle\zeta;\zeta'\rangle$ behaves much like the wave function in the ordinary interpretation of quantum theory. The difference is that the sharing amplitude is much more complex than the wave function by being a function of eight (6 spatial + 2 spin) coordinates. For singlet states, this complexity can be simplified somewhat by the fact that the dependence of $\langle\zeta;\zeta'\rangle$ on the spin coordinates is $\delta_\sigma\sigma' = \alpha(\sigma)\alpha^*(\sigma') + \beta(\sigma)\beta^*(\sigma')$ so that the amplitude is a function of six spatial coordinates. To make the amplitude suitable for the visualization purposes, one coordinate ζ' can be fixed. Call this variable the fixed point. By fixing one point and restricting the system to a singlet, the amplitude $\langle\zeta;\zeta'\rangle$ remains a function of three spatial coordinates. In terms of natural orbitals $\varphi_m(\zeta)$, the amplitude may be written as

$$\langle\zeta;\zeta'_{\mathrm{fixed}}\rangle = \sum_m \varphi_m(\zeta)a_m$$

where $a_m = \sum_m \rho_m^{1/2}\varphi_m^*(\zeta')$. By writing the natural orbitals as linear combinations of atomic orbitals, the (one fixed point) sharing amplitude may be interpreted in terms of traditional concepts such as hybrid orbitals. Therefore, the molecular orbital and valence bond terminologies are quite convenient for describing the (one fixed point) sharing amplitudes in this section.

What was the criterion for choosing the fixed points of the sharing amplitudes? As a quantitative measure of the electron delocalization from one region to the other in atoms and molecules, the delocalization index was constructed by integrating one point of the point−point sharing index over one region and the other over the other region.[1] The delocalization indices from spherical volumes of various radii centered on the phosphorus nucleus to the volumes outside those regions show remarkably well-defined shell structure.[28−30] The delocalization shell structure in the phosphorus is given in Figure 1. The delocalization shell structure displays spatial regions from which electrons are greatly delocalized and regions determined by the intershell minima in which electrons are essentially localized. The delocalization index is quite different in concept from the other indicators of the shell structure. Figure 1 also shows that the valence shell of the phosphorus is more than 0.96 au away

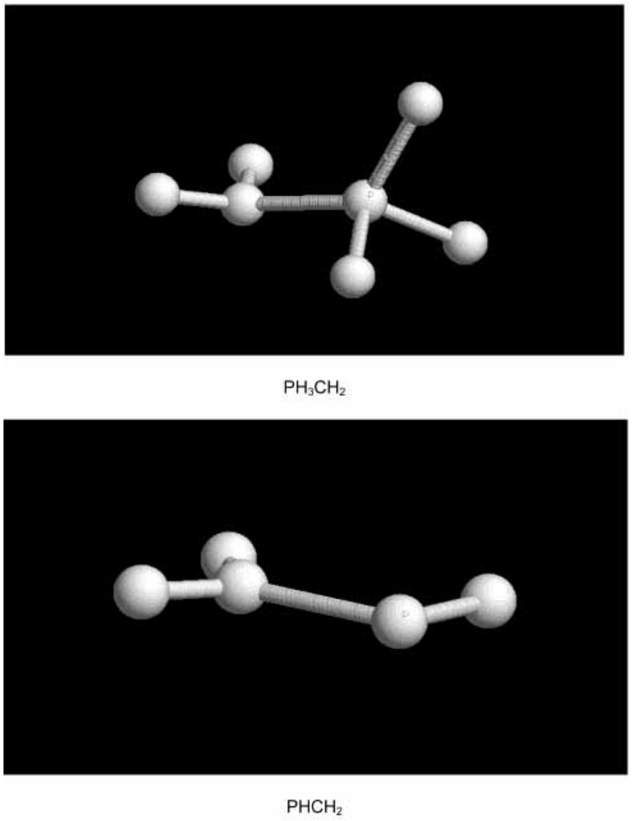

Figure 2. Optimized geometries of the complexes PH_3CH_2 and $PHCH_2$.

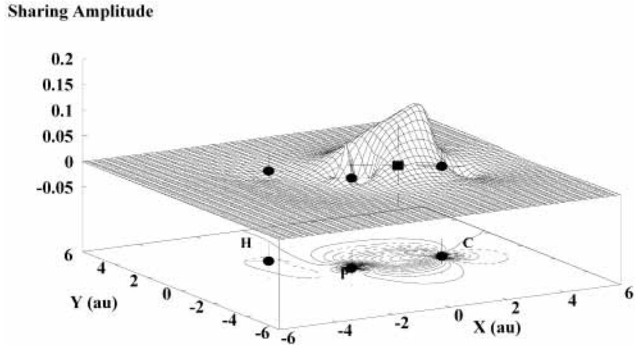

Figure 3. Cut of the sharing amplitude in the complex PH_3CH_2.

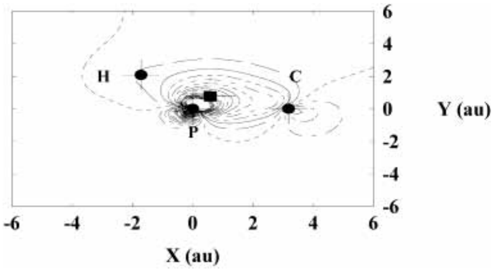

Figure 4. Contour map of the sharing amplitude in PH_3CH_2.

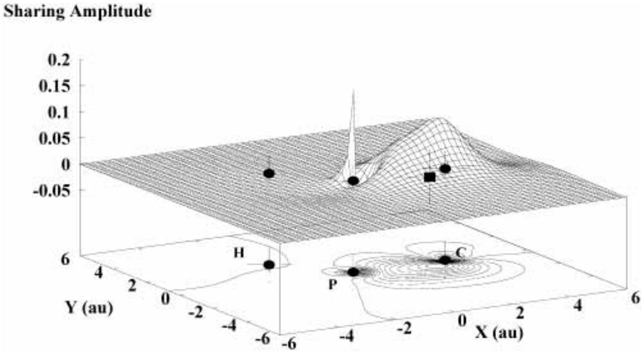

Figure 5. Cut of the sharing amplitude in the complex PH_3CH_2.

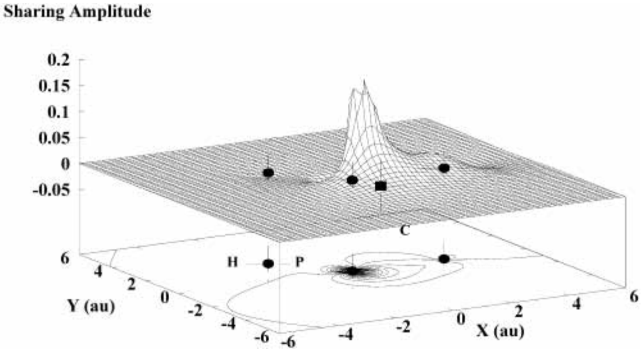

Figure 6. Cut of the sharing amplitude in the complex PH_3CH_2.

from the nucleus. The last maximum corresponding to the region within the valence shell is at 1.98 au from the center of the nucleus. Therefore, the positions of the fixed points are located in the valence region. In this fashion, the delocalization index is directly employed to ferret out connections between the electron delocalization and the chemical behavior of the ylides of phosphorus. Some particular positions of the fixed points in the valence region of the phosphorus used in this section presumably allow qualitative descriptions of the (one fixed point) sharing amplitudes including the mixing of all the valence electrons.

The relaxed first-order density matrixes produced by the GAUSSIAN 92[31] at the MP2/6-31++G** level of approximation have been used. The optimized molecular geometries of the complexes PH_3CH_2 and $PHCH_2$ are given in Figure 2, which is produced by the program RASMOL.[32] Note that the unique proton bonded to the phosphorus in PH_3CH_2 is bent to the same side as the CH_2 group with respect to the P−C internuclear axis. Note also that the CH_2 group is planar in the complex $PHCH_2$.

One coordinate is fixed in the figures given below. The variable coordinate is restricted to be in a two-dimensional plane. The fixed point is designated by a filled square while the filled circles present the positions of the atoms in plane. The sharing amplitudes of $PHCH_2$ and PH_3CH_2 are analyzed with respect to the fixed points. From the left to the right, the planes of Figures 3−7 displaying the PH_3CH_2 sharing amplitudes contain the unique hydrogen on phosphorus, the phosphorus (in the center of the plane) and the carbon nucleus. The coordinates of the nuclei in the plane expressed in atomic units are C (3.18, 0), P (0, 0), and H (−1.71, 2.08).

The sharing amplitude in the ylide PH_3CH_2 with the fixed point at the distance of 2.1 au from the phosphorus toward the carbon lying under the highest peak is given in Figure 3. The contour lines ranging from −0.2 to 0.3 with the increment of 0.01 are given at the base of Figure 3. The shape of the sharing amplitude is qualitatively similar to a tight orbital on the carbon extending up to the beginning of the valence region of the phosphorus indicating the delocalization of an electron over the region. The shape of the amplitude looks very much like a distorted p-type function exhibiting a more lone-pair character as well. Note that the position of the fixed point is closer to the carbon nucleus than to the phosphorus.

The next choice of the position of the fixed point is 1 au from the phosphorus nucleus. From the left to the right, the nuclei in the plane are the unique hydrogen bonded to the

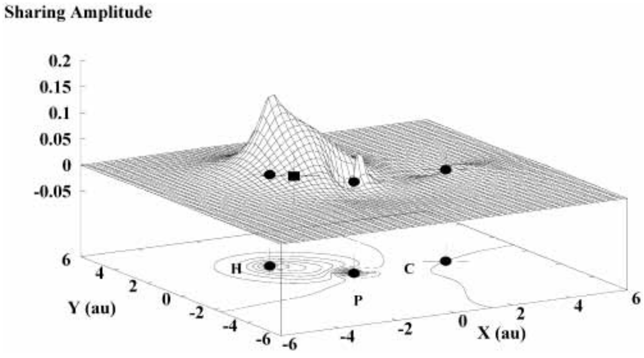

Figure 7. Cut of the sharing amplitude in PH_3CH_2.

phosphorus, the phosphorus and the carbon. The contour plot shows the projection of the fixed point in the *XY* plane. The contour lines ranging from −0.4 to 0.2 with the increment of 0.01 are given in Figure 4. It is clear that the sharing amplitude shows a more diffuse character on the phosphorus. The contour lines extending to the unique proton illustrate electron delocalization over the carbon, phosphorus and hydrogen (attached to the phosphorus) basins. Viewed together, Figures 3 and 4 can be qualitatively observed to exhibit two components of a popularly called "bent" bond.

The sharing amplitude in the ylide PH_3CH_2 with the fixed point at about 2.23 au from the phosphorus is given in Figure 5. The contour lines ranging from −0.2 to 0.3 with the increment of 0.01 are given on the base of Figure 5. The sharing amplitude, as a strongly distorted p-type function, is tightly placed on the carbon spreading all over the valence region into the vicinity of the phosphorus.

The sharing amplitude in the ylide PH_3CH_2 with the fixed point lying under the highest peak is given in Figure 6. Note that the fixed point is about 0.97 au from the phosphorus. The contour lines ranging from −0.4 to 0.2 with the increment of 0.01 are given in Figure 6. A more diffuse character displayed by the amplitude on the phosphorus is clear. The diffuse character of the sharing amplitude viewed along with the tight one on the carbon (Figure 5) can be looked at as a bent or popularly called a "banana" bond in a more traditional sense.

The sharing amplitudes given in Figures 3 and 4 are not equivalent to those given in Figures 5 and 6, as expected because of nonplanarity of the CH_2 group. The first pair of the amplitudes (Figures 3 and 4) has a more diffuse character on the phosphorus nucleus than that displayed by Figures 5 and 6 and lies on the side where the two hydrogens on carbon are bent above the internuclear axis.

The sharing amplitude with the fixed point at 2 au away from the phosphorus toward the unique proton is given in Figure 7. The contour lines within a range from −0.1 to 0.4 with the increment of 0.02 are given on the base of the same figure. Apparently, the P−H sharing amplitude tends to stay away from the P−C sharing amplitudes considered above as much as possible. In a more traditional sense, this exhibited property of the P−H sharing amplitude essentially lowers the electron repulsion between the P−H bond and the P−C bonds. The carbon atom as an anion has a high energy HOMO. On the other hand, the phosphorus group as a cationic has stable unoccupied orbitals. The carbon atom is certainly able to donate into these unoccupied orbitals. A relatively large the C−P−H bond angle may be a consequence of the back-bonding.

The sharing amplitudes in the complex $PHCH_2$ with the fixed points located in the valence region of the phosphorus are given in Figures 8, 9, 10, 11, and 12, respectively. The fixed point is

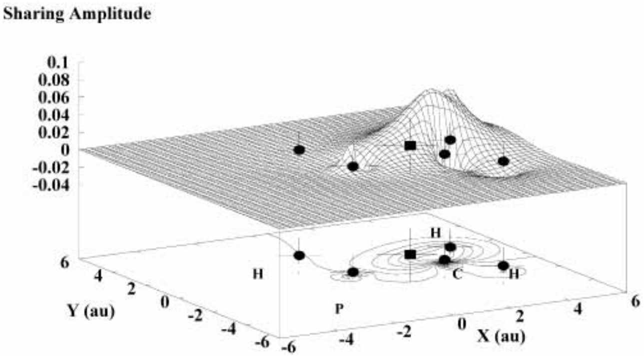

Figure 8. Cut of the sharing amplitude in the complex $PHCH_2$.

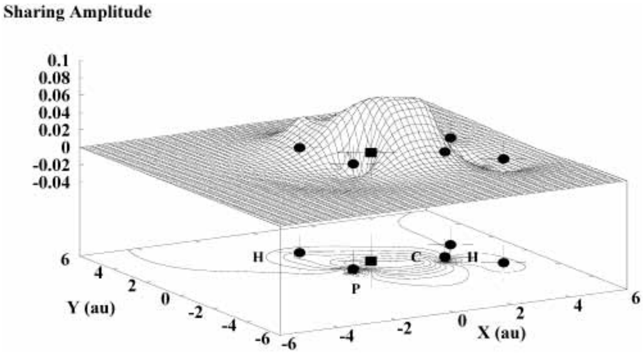

Figure 9. Cut of the sharing amplitude in the complex $PHCH_2$.

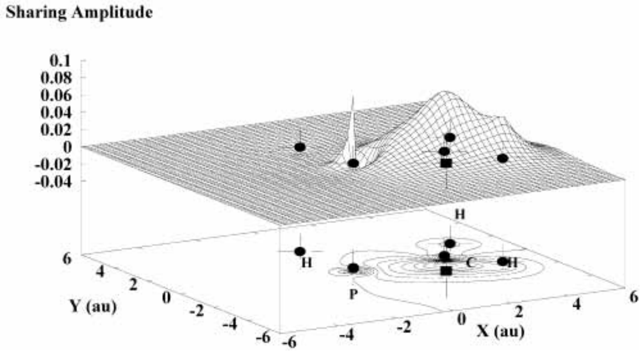

Figure 10. Cut of the sharing amplitude in the complex $PHCH_2$.

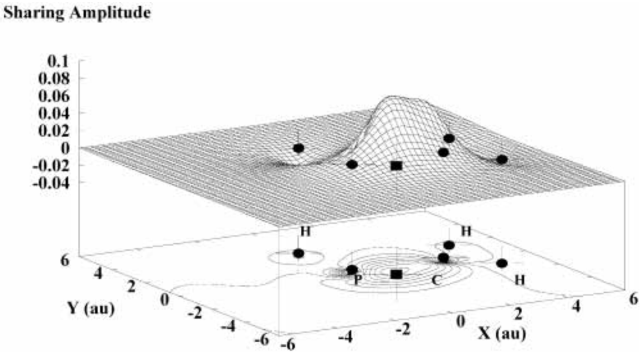

Figure 11. Cut of the sharing amplitude in the complex $PHCH_2$.

given by a filled square while filled circles present the nuclei in the plane of the cut. From the left to the right, the nuclei in the planes of the Figures 8−12 are the hydrogen (bonded to the phosphorus), phosphorus (in the center of the plane), and carbon. The coordinates of the nuclei in the plane of the cut expressed in atomic units are C (3.17, 0), P (0, 0), and H (−0.33, 2.65). The first fixed point is at 3.23 au from the phosphorus (Figure 8) and the second is 2.8 au from the phosphorus (Figure

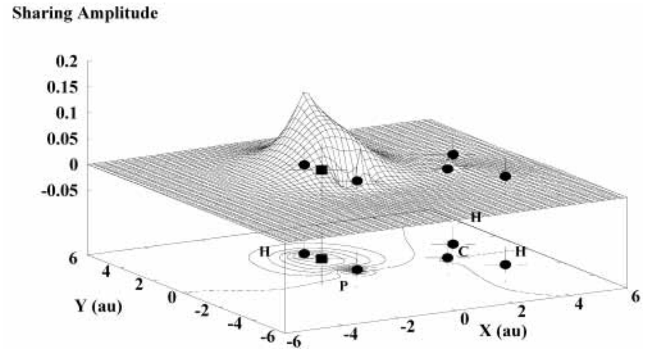

Figure 12. Cut of the sharing amplitude in the complex $PHCH_2$.

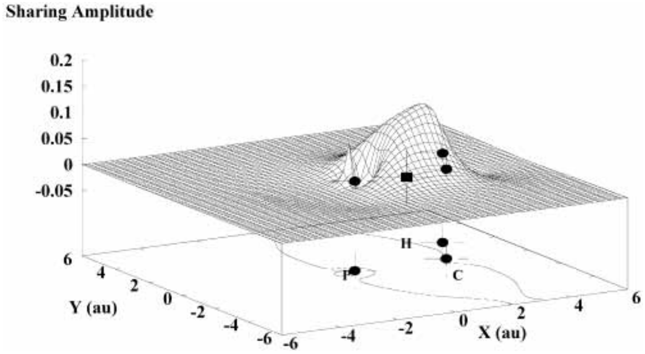

Figure 13. Cut of the sharing amplitude in the complex PH_3CH_2.

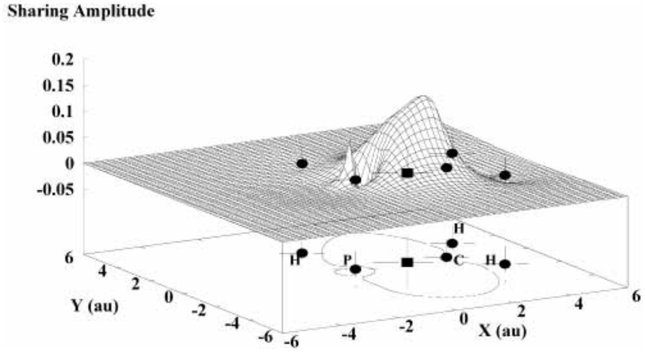

Figure 14. Cut of the sharing amplitude in the complex $PHCH_2$.

10). The third fixed point is 1.61 au (Figure 9) and the fourth is 1.37 au (Figure 11) away from the phosphorus, respectively. The fifth fixed point is at 1.80 au from the phosphorus toward the proton (Figure 12).

The sharing amplitudes given in Figures 8 and 10 are tightly placed on the carbon. Note that the two amplitudes (Figures 8 and 10) on carbon are similar to one another spreading into the vicinity of the phosphorus. Note also that the amplitude given in Figure 9 displays a substantially larger delocalization of an electron in $PHCH_2$ than that in PH_3CH_2 (Figure 4) not only all over the valence region of the phosphorus, but also over the hydrogen basin attached to the phosphorus. This has been quantitatively accounted for in $PHCH_2$ and PH_3CH_2 by the values of the P−C interbasin sharing indices in ref 2. The P−H sharing amplitude (Figure 12) tends away from the P−C sharing amplitudes (Figures 8−11) decreasing the electron repulsion between the P−H bond and the P−C bonds. The C−P−H angle in the complex $PHCH_2$ is also different from that in PH_3CH_2.

An additional detail needs to be elaborated. Figures 13 and 14 display the sharing amplitudes of the PH_3CH_2 and $PHCH_2$, respectively, with the fixed points chosen to be almost along the P−C bond axis. From the left to the right, the planes of Figures 13 and 14 contain the phosphorus nucleus (in the center), the carbon and the hydrogen (on carbon), respectively. The fixed point in Figure 13 is at 1.82 au from the phosphorus while that in Figure 14 is at 1.58 au away from the phosphorus.

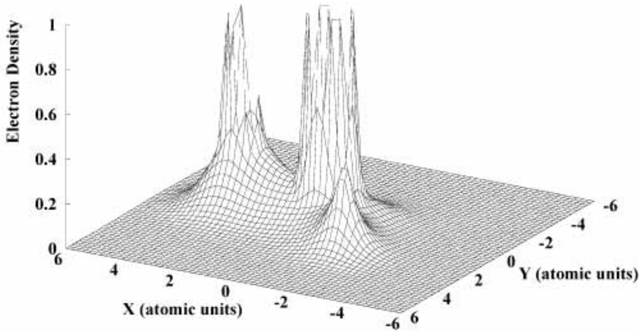

Figure 15. Cut of the electron density in the complex PH_3CH_2. Contrast the electron density in the region between the carbon and the phosphorus with the volume−point sharing index in the same region given in Figure 16.

Note the shapes of the two nodal lines in the immediate vicinity of the carbon as well as their shapes moving away from the carbon nucleus. The nodal lines are very similar to one another in the immediate vicinity of the carbon. Then, moving slowly away from the carbon nucleus, to the right and to the left, the PH_3CH_2 nodal line is straightening out significantly in comparison to the $PHCH_2$ nodal line. A substantial increase of the 2p orbital character, in the case of PH_3CH_2, is clear. This difference has been precisely reflected in the P−C interbasin sharing indices quantitatively (ref 2), 0.92 for PH_3CH_2 (0.87 for a classical single bond), and 1.30 for $PHCH_2$ (1.54 for a classical double bond).

IV. Volume−Point Sharing Indices

A dissection of sharing can be obtained by the volume−point sharing index when one point of the point−point sharing index is integrated over a single primary basin. By this, we get an insight into the sharing of an electron between a basin and all points in space. This volume−point sharing index provides information about the distribution of sharing of an electron.

Two existing descriptions of the actual electron-density distribution in the P−C bonds are that (1) there are two electron pairs as a result of the σ bond between P and C and a π back-bond between a p orbital on carbon and a antibonding orbital on phosphorus toward the other ligands and (2) there are two “banana” bonds from P to C. A common point to both of these understandings is that the electron density distribution is strongly skewed toward carbon. Let contrast the cut of the electron density in the region between the carbon and the phosphorus in PH_3CH_2 with the volume−point sharing index in the same region.

A slice of the electron density in the complex PH_3CH_2 is shown in Figure 15. The plane of cut contains the carbon nucleus at the left; the phosphorus nucleus, in the center of the plane; and the unique proton which is bonded to the phosphorus sitting under the least intense peak at the right. The coordinates of the nuclei in the plane of the cut expressed in atomic units are C (3.18, 0), P (0, 0), and H (−1.71, 2.08).

The $x = 2.6$ au line is roughly the boundary of the carbon basin. If the lines in the range from $x = 2.2$ au to $x = 2.4$ au are followed in Figure 15, note that the electron density “leans” toward the carbon nucleus. The electron density in this region reflects relative electro negativities of the two elements, which

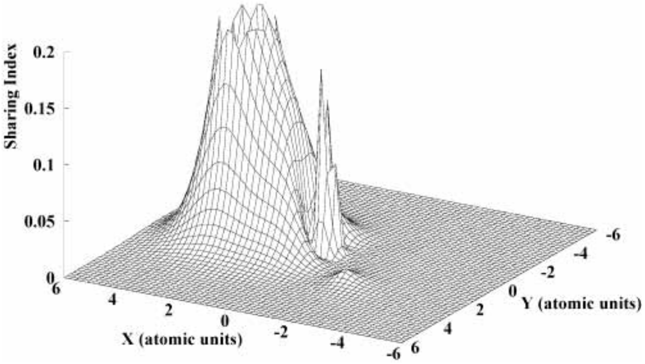

Figure 16. Cut of the volume−point sharing index in the complex PH_3CH_2. The principal basin is the carbon basin.

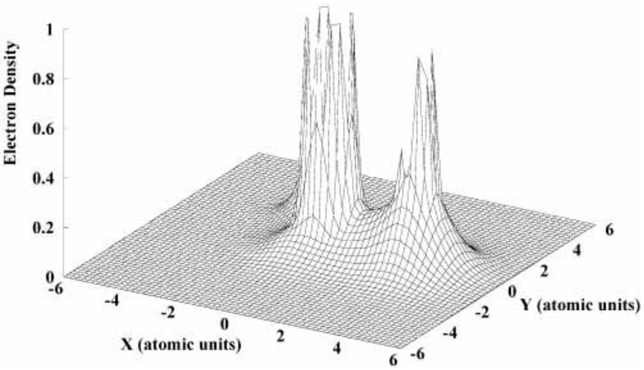

Figure 17. Cut of the electron density in the complex PH_3CH_2. Contrast the electron density in the region between the carbon and the phosphorus with the volume−point sharing index in the same region given in Figure 18.

are 2.5 for C, and 2.1 for P. The dividing surface between the PH_3 and the CH_2 groups intersects the plane of the cut close to the line for which $x = 1.2$ au.

A slice of the volume−point sharing index from the primary carbon basin in the complex PH_3CH_2 is shown in Figure 16. The plane of cut is the same as that used for the electron density in Figure 15. Note also that the vertical scale of the cut of the volume−point sharing index is chosen to be different from that of the electron density (Figure 15).

Consider the behavior of the sharing index along a straight line $x = 2.6$ au. The $x = 2.6$ au line which was about the boundary of the carbon basin in Figure 15, lies within the carbon basin in Figure 16. There is a large and broad peak at the primary nucleus. Near the primary carbon basin, the volume−point sharing index in Figure 16 does not resemble the electron density in Figure 15. The volume−point sharing index also shows that the lines followed in Figure 16, from $x = 2.2$ au to $x = 2.4$ au, are within the carbon basin. The sharing index falls off somewhat gradually before a precipitous decline to a very small value just before a rise to a peak at the phosphorus nucleus. The extremely small values of the sharing index as it approaches the immediate vicinity of the phosphorus indicate that there may be a node in the underlying sharing amplitudes. Recall from part II that the nodes formed in the sharing amplitudes appear only as remnants of nodes in the volume−point sharing indices.

In addition, the delocalization shell structure in phosphorus given in Figure 1 shows that the valence region is more than 0.96 au away from the phosphorus nucleus. Note the circular shape of the minimum of the sharing index having the radius of about 1.7 au around the phosphorus nucleus in the center of the plane, as given in Figure 16. The value of 1.7 au is within the valence shell. The circular shape indicates a remnant of a 3s or a 3p contribution.

Beyond the phosphorus nucleus toward the unique proton, the sharing index falls off to an extremely small value in the immediate vicinity of the phosphorus nucleus indicating the presence of another node. This very small value extends until a rise to a peak at the hydrogen nucleus. Although this peak is lower than that at P, it is still significant in terms of showing clearly the delocalization of an electron over the hydrogen basin as well. This delocalization from the carbon basin to the hydrogen basin was reflected in ref 2 by the value of 0.13 for the sharing between the carbon and hydrogen basin on phosphorus (Table 2). In addition, this substantial delocalization of an electron over the carbon, phosphorus and hydrogen basins in PH_3CH_2 is probably related to the special stabilization of the carbanion.

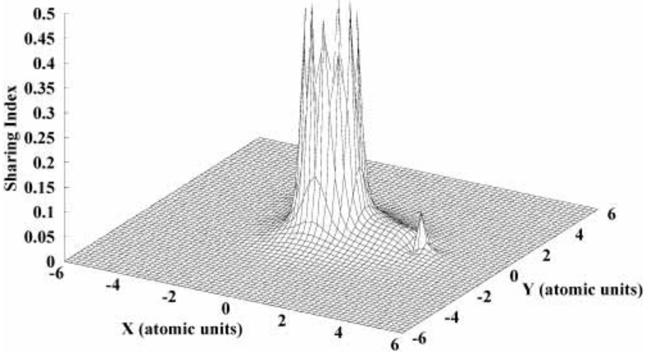

Figure 18. Cut of the volume−point sharing index in the complex PH_3CH_2. The principal basin is the phosphorus basin.

In contrast to the cut of the electron density in Figure 15, if the $x = 1.2$ au line is followed on the surface of the sharing index in Figure 16, the line is found to be considerably to the left toward the carbon, that is, skewed toward carbon.

A slice of the electron density in the complex PH_3CH_2 with view rotated 180° counterclockwise around the z-axis with respect to Figure 15 is shown in Figure 17. The plane of the cut contains the same nuclei as Figure 15, but having the carbon atom at the right. From the right to the left, the coordinates of the nuclei in the plane of the cut expressed in atomic units are C (3.18, 0), P (0, 0), and H (−1.71, 2.08). Figure 17 is very convenient to see clearly that the $x = 1.2$ au line represents roughly the dividing surface between the PH_3 and the CH_2 groups in the ylide, as established in Figure 15.

A slice of the volume−point sharing index from the primary phosphorus basin in the complex PH_3CH_2 is shown in Figure 18. The plane of cut is the same as that used for the electron density in Figure 17. Note also that the vertical scale of the cut of the volume−point sharing index is different from that of the electron density (Figure 17) because of physically different definitions of the two quantities.

It is important to note that near the primary phosphorus basin, the sharing index mimics that of the electron density: there is a large peak at the phosphorus nucleus. If the $x = 1.2$ au is followed in Figure 18, the sharing index exhibits a shoulder. Then, the sharing index rapidly falls off to an almost constant value until the immediate vicinity of the carbon nucleus is reached where the index has a decline to an extremely small value before a rise to a peak at the carbon nucleus. The minimum of the sharing index in the vicinity of the carbon nucleus is probably a remnant of a node formed in the underlying sharing amplitude.

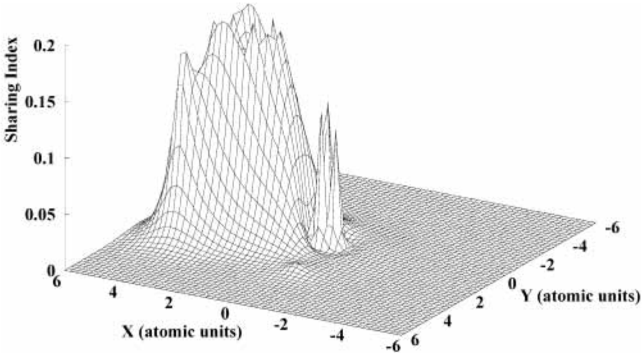

Figure 19. Cut of the volume−point sharing index in the complex $PHCH_2$. The principal basin is the carbon basin.

A slice of the volume−point sharing index from the primary carbon basin in the complex $PHCH_2$ is shown in Figure 19. The plane of cut contains the carbon nucleus at the left; the phosphorus nucleus, in the center of the plane; and the proton which is bonded to the phosphorus sitting under the least intense peak at the right. The coordinates of the nuclei in the plane of the cut expressed in atomic units are C (3.17, 0), P (0, 0), and H (−0.33, 2.65).

The sharing index displays a shape very similar to that in PH_3CH_2 given in Figure 16 qualitatively, especially in terms of the electron delocalization over the C, P, and H (attached to the phosphorus) basins. The clear distinction to the sharing index in PH_3CH_2 given in Figure 16 is much broader peak at the primary carbon basin. The fact has been quantitatively reflected in the values of the P−C interbasin sharing indices in ref 2: 1.30 for $PHCH_2$ (Table 3) versus 0.92 for PH_3CH_2 (Table 2). It is also in agreement with the larger charge separation between the phosphorus and the carbon in PH_3CH_2 (−1.17 for C and +2.97 for P) than that in $PHCH_2$ (−0.90 for C and +1.42 for P), as given in Table 4. Besides, the circularly shaped minimum of the sharing index, as a remnant of a node, seems to encompass more the phosphorus nucleus in the center of the plane in Figure 19 than that in Figure 16.

The cut of the volume−point sharing index in the complex $PHCH_2$ is very similar to that of ethylene.[25] There has also been a controversy about the best description of the ethylene double bond, that is, two equivalent bent banana bonds or a σ and a π bond. Kaldor[33] has found the “better” description to be the two equivalent banana bonds energetically.

All the figures presented in this article, except Figure 2, have been produced by GNUPLOT.[34]

V. Conclusions

The sharing amplitudes and the sharing indices[1] offer the needed tools to describe the behavior of a single electron in many electron systems. The sharing quantities are invariant under transformations of the orbitals in terms of which the wave function is expressed and are independent of the sufficiently complete basis set. As such they are physically meaningful.

This paper supplemented by ref 2 provides a consistent picture regarding the nature of the P−C bonds in simple phospho-ylides. A new insight is based on the considerations of the bonds between the groups constituting λ^3 and λ^5 carbon phosphorus compounds.

The beauties of the description of electron behavior developed by R. L. Fulton[1] are apparent because many contacts with more traditional (and noninvariant) modes of interpreting electron behavior can be made.

Acknowledgment. The author thanks Professor Robert L. Fulton for many constructive ideas.

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