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COMMENTS

Comment on "Qualitative Characterization of the P−C Bonds in Ylides of Phosphorus"

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In a recent paper Mitrasinovic[1] gave an analysis of the bonding in some phosphorus ylides using concepts introduced by the present author.[2] Unfortunately, the author did not adequately acknowledge the people responsible for the initial, but substantial, work on the analysis. These were Justin Oelgoetz, an undergraduate previously working with the present author, and Pablo Perhacs, a doctoral student who received his Ph.D. under the direction of the present author. The work was, in part, included in a proposal that was submitted by the present author to the National Science Foundation. To indicate the direction of a part of his research Mitrasinovic was supplied with that portion of the proposal dealing with the phosphorus ylides. This material included the information in Tables 1−4 of ref 1 and plots of the electron density and the volume-point sharing indices in PH_3CH_2. Mitrasinovic also did not reference the fact that the material in the paper was taken from his Ph.D. dissertation done under the direction of the present author and submitted to the Department of Chemistry and Biochemistry.

In addition, the plot of the delocalization index for P given in Figure 1 of ref 1 has an incorrect behavior at large R. The delocalization index $\Delta(R)$ gives the sharing of an electron between an inner spherical volume of radius R centered on the nucleus and the outer volume.[3] In terms of atomic overlap matrices,[4] $\Delta(R)$ is given by

$$\Delta(R) = \sum_{m,n} \nu_m^{\;1/2} \nu_n^{\;1/2} (\varphi_m,\varphi_n)_{|r|\le R} (\varphi_n,\varphi_m)_{|r|>R} \tag{1}$$

ν_m is the occupation number of the mth natural spin−orbital[5] $\varphi_m(\zeta)$ and $(\varphi_m,\varphi_n)_{|r|\le R}$, an element of the atomic overlap matrix, is given by the integral

$$(\varphi_m,\varphi_n)_{|r|\le R} = \int_{|r|\le R} \mathrm{d}\zeta \; \varphi_m^*(\zeta)\; \varphi_n(\zeta)$$

with a similar integral over the range $|r| > R$ for $(\varphi_m,\varphi_n)_{|r|>R}$. ζ represents the three spatial coordinates and the one spin coordinate.

The upper curve in the present Figure 1 gives the result of a calculation of $\Delta(R)$ for the phosphorus atom using the GAUSSIAN98 suite of programs[6] with the 6-31++G** basis set at the QCISD level of approximation and using a version of PROAIMV[7] modified such that the radius of the β sphere never exceeds the radius R. (The lower curves are discussed below.) For large R the delocalization index is found to decrease with increasing R in a much slower fashion than that given by Mitrasinovic in ref 1.

The large R behavior of $\Delta(R)$ can be quite simply found if the asymptotic behavior of the dominant, most slowly decreasing natural spin−orbital is known. This may be found as follows. The ground state of a phosphorus atom is $^4S_{3/2}$. Because the total orbital angular momentum is a good quantum number which vanishes for this state, the contributions from different orbital angular momentum do not interfere in the construction of $\Delta(R)$. The argument is the following:

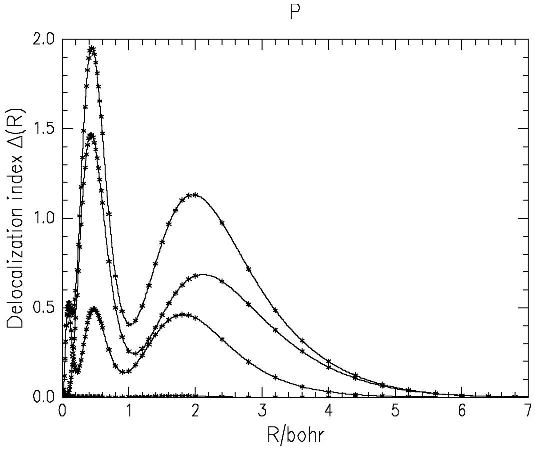

Figure 1. $\Delta(R)$ and $\Delta_l(R)$'s of a phosphorus atom.

The vanishing of the total orbital angular momentum implies that the total wave function is simultaneously an eigenfunction of all three components of the total orbital angular momentum. As a consequence, the single particle density matrix, and hence the sharing amplitude, commutes with each component of the single particle angular momentum and therefore with the square of the angular momentum. As a result, the sharing amplitude has the structure

$$\langle \zeta;\zeta' \rangle = \sum_{l,m} Y_{lm}(\theta,\varphi)\; A_l(r\sigma;r'\sigma')\; Y_{lm}^*(\theta',\varphi') \tag{2}$$

with $A_l(r\sigma;r'\sigma')$ a function of the indicated variables which is independent of m. $\langle \zeta;\zeta' \rangle$ therefore contains no cross terms containing different $Y_{lm}(\theta,\varphi)$'s. Because the inner and outer regions of integration are spherical, the contributions $\Delta_l(R)$ of the different angular momentum l to $\Delta(R)$ are additive with no interference terms

$$\Delta(R) = \sum_l \Delta_l(R) \tag{3}$$

with

$$\Delta_l(R) \equiv (2l+1) \sum_{\sigma,\sigma'} \int_{|r|\le R} \mathrm{d}r\; r^2 \int_{|r|>R} \mathrm{d}r'\; r'^2 |A_l(r\sigma;r'\sigma')|^2$$

The lower three curves of Figure 1 give the contributions, from top to bottom, of the angular momentum $l = 1, 0, 2$ to $\Delta(R)$. The $l = 2$ contribution nearly vanishes. The $l = 0$ contribution gives three peaks, while the $l = 1$ contribution has but two peaks. The rightmost maximum is from the $l = 1$ contribution, this clearly having the slowest falloff and extending well beyond the $l = 0$ contributions. We therefore take the spin−orbitals which contribute to this region to have a principal quantum

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number of 3 and angular momentum 1 (a 3p orbital). We therefore suppose the large r behavior (ignoring the angular factors) to be of the form

$$r^2 e^{-\beta r}$$

giving a contribution of

$$\text{const} \times \left\{ \sum_{n=0}^{6} \frac{6!}{(6-n)!} \frac{R^{6-n}}{(2\beta)^{n+1}} \right\} e^{-2\beta R} \tag{4}$$

to $\Delta(R)$. The large R behavior of $\Delta(R)$ is therefore a polynomial in R times a simple exponential decrease with increasing radius. This has a much slower falloff with increasing R than that given in ref 1. The rapid falloff given in ref 1 is inexplicable.

References and Notes

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