

## The localized pair model of electronic structure analysis

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### ABSTRACT

We introduce the localized pair model of electronic structure analysis and propose the two-electron reduced density matrix as an important interpretive tool in chemistry. Interelectronic probability distributions in position and momentum space are calculated for individual localized molecular orbitals corresponding to intuitive chemical features such as lone pairs and chemical bonds. It is demonstrated that these may be interpreted as the distribution of electrons within a chemical bond or lone pair and we refer to this model as the *localized pair model* of electronic structure analysis. Specifically, the Hartree–Fock level of theory is employed in conjunction with a completely uncontracted 6-311G (d,p) basis set to construct our localized orbitals. Spherically averaged position and momentum intracules are calculated for each orbital and we present results for orbitals of p-block hydrides, saturated main group compounds, fluorinated species, N → B dative structures, and small cyclic molecules. We find that our analysis generally agrees quite well with intuitive predictions based on bond lengths and electronegativities of the bonded atoms. However the trends in the data cannot be predicted using the bond length or electronegativity alone, which demonstrates the unique features of this model.

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### 1. Introduction

In their influential book, “Reduced Density Matrices: Coulson’s Challenge”, John Coleman and Vyacheslav Yukalov eloquently describe the impressive predictive power contained within the second order reduced density matrix, or 2-matrix as it is commonly known, given by [1]

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{n(n-1)}{2} \int |\Psi(\mathbf{x}_1, \dots, \mathbf{x}_n)|^2 ds_1 ds_2 d\mathbf{x}_3 \dots d\mathbf{x}_n \quad (1)$$

where  $\mathbf{x}_i = (\mathbf{r}_i, s_i)$  denotes the combined position and spin coordinates of electron  $i$ . They discuss the attractive prospect of employing the 2-matrix as the fundamental quantity for the general prediction of the energy levels of chemical systems. Of course the concept of an electron pair as a fundamental entity in chemistry is ubiquitous and it is therefore a natural choice for electronic structure prediction. Here we offer a complementary application of the so-called 2-matrix for the *analysis* of electronic structure. We argue that the 2-matrix can serve as an important interpretive tool in quantum chemistry and we show briefly that ubiquitous concepts such as the chemical bond may be scrutinized in new and intuitive ways with some creative applications of it.

Since the days of Lewis [2], chemists have been enamoured with the concept of a localized electron pair to represent the now intuitive features of electronic structure such as the so-called lone pair

and the chemical bond itself. Despite its simplicity, the Lewis model yields an impressive wealth of predictive ability in terms of molecular structure [3] and chemical properties and is a universal concept in the chemical literature. Is there a way to link the essence of the Lewis model to the quantum mechanical description of electron pairs? Within the orbital approximation in quantum mechanics, the delocalized canonical molecular orbitals (CMOs) of a general chemical system bear little resemblance to the features of a Lewis structure. In contrast however, CMOs are amenable to a unitary transformation to afford the less well-known [4–10] *localized* molecular orbitals (LMOs)[11–13]. These are an equivalent description of electronic structure and yield intuitive and highly transferable orbitals that can be said to represent individual bonds, lone pairs, and core electrons (*vide infra*). It is within the space of LMOs then, that we should find such a link.

While the Lewis model can be remarkably powerful in its prediction of molecular structure and some properties; it yields little information regarding the distribution of the electrons themselves. Are electrons within a particular pair generally close together, or far apart? Do they move quickly or slowly? How do these distributions change with the chemical environment? Most importantly, do these quantities relate to observable chemical properties? We seek to address these important questions in the present article. To do this, we calculate interelectronic probability distributions, also known as intracules, for particular LMOs. A *position* intracule,  $P(u)$ , is the probability distribution for  $u = |\mathbf{r}_2 - \mathbf{r}_1|$ , and therefore yields the likelihood of a pair of electrons being separated by a distance  $u$

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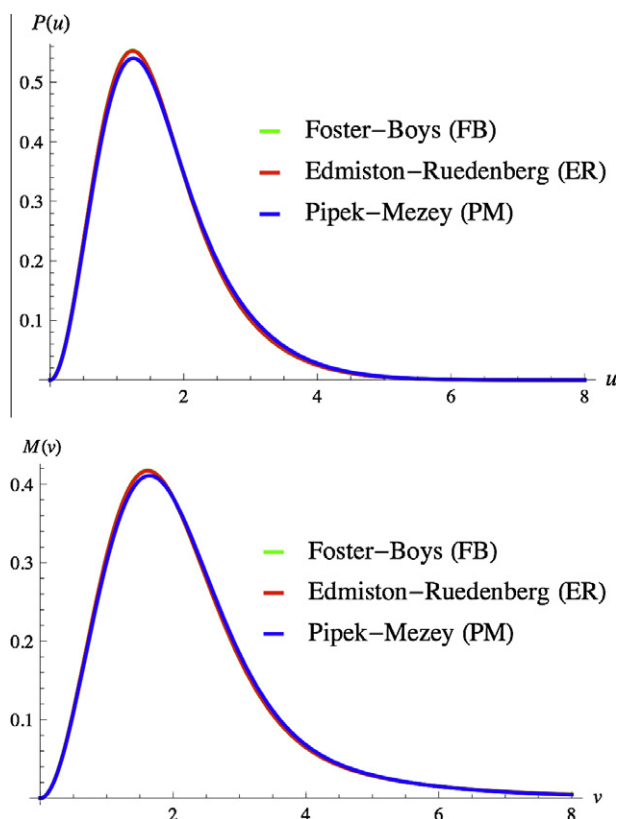


Fig. 1. A comparison of the position (top) and momentum (bottom) intracules for the water O–H bond. Note the FB (green) result is not visible, as it coincides with the ER (red) result. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$P(u) = \int \rho_2(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{r}_{12} - \mathbf{u}) d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_u \quad (2)$$

In the above expression,  $\delta$  is a Dirac delta function and  $d\Omega_u$  indicates integration over the angular components of the  $\mathbf{u}$  vector. As such,  $P(u)$  is often referred to as the “spherically averaged” intracule density.

Likewise, the spherically averaged momentum intracule,  $M(v)$ , is the probability distribution for  $v = |\mathbf{p}_2 - \mathbf{p}_1|$  (where  $\mathbf{p}_i$  describes the position of electron  $i$  in momentum space), and describes the relative momenta of two electrons. We can compute this distribution in an analogous fashion as  $P(u)$  by replacing  $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$  with its momentum space analogue,  $\pi_2(\mathbf{p}_1, \mathbf{p}_2)$  [14,15]

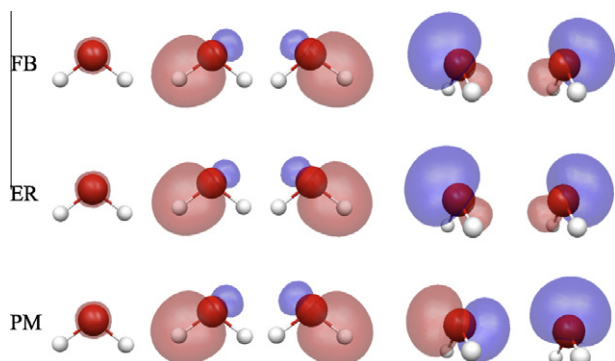


Fig. 2. A comparison of the five molecular orbitals of water determined with each of the three localization procedures. The contour value of these orbitals is 0.10 a.u., with the exception of the core orbital on the far left, whose contour value is 0.03 a.u. to make it visible.

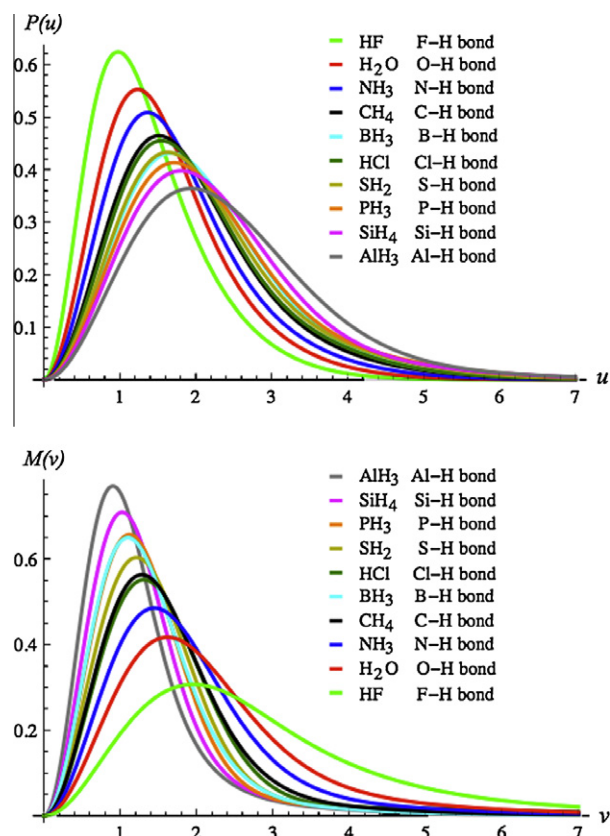


Fig. 3. A comparison of the position (top) and momentum (bottom) intracules of first and second row hydride X–H bonds.

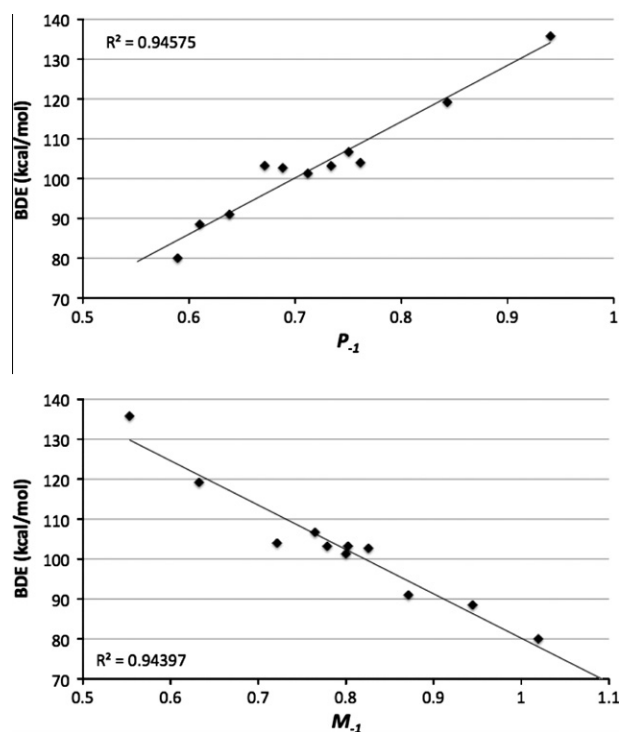


Fig. 4. A plot of the experimental bond dissociation energies (kcal/mol) of the p-block hydrides versus the first inverse moment of the position and momentum bond intracules.

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