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Maximum Probability Domains in the Solid-State Structures of the Elements: the Diamond Structure

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In Memory of Professor Hans Georg von Schnering

Abstract. Regions of space are defined to maximize the probability to find two electrons in it. They can be interpreted as regions where Lewis' electron pairs are most likely to be found. These maximum probability domains (MPDs) provide information similar to that obtained from the electron localization function (ELF), but is not identical to it. The elements in the diamond structure provide examples for a comparison.

Introduction

Professor Hans Georg von Schnering did not only understand the importance of theory, he actively supported it. For some time, one of us (A.S.) strongly interacted with him, and it is now clear that one of the tools, which we consider to be very useful to interpret bonding in crystals, the electron localization function (ELF),[1] would have never had the success it had without his extraordinary chemical insight that made von Schnering proposing relevant applications for it. In this paper, we continue a line, which would have been, we believe, in a spirit he would have liked. We even borrowed the title of the present contribution from a paper of *von Schnering* and co-workers: "Electron Localization in the Solid-State Structures of the Elements: the Diamond Structure",[2] a paper where, for the first time, ELF was applied to crystalline structures.

ELF is a function, defined in each point in three-dimensional space, designed to get maximal values in regions where electron pairs are localized. One can join all points around a maximum to form a so-called basin, by following the uphill paths from each of the points. All points leading to the same maximum, belong to the same basin. In this paper the same class of electronic systems is studied, but a new technique is used to find the regions of space where electron pairs localize. These regions are called maximum probability domains, and are defined as the regions of space for which the probability to find a pair of electrons is maximal. In order to be more

precise, let us consider an electronic system described by a wave function Ψ. The probability to find ν and only ν electrons out of N in a three-dimensional region Ω is given by

$$p_\nu(\Omega) = \binom{N}{\nu} \int_\Omega dx_1...dx_\nu \int_{\bar\Omega} dx_{\nu+1}...dx_N |\Psi(x_1, ..., x_N)|^2 \quad (1)$$

where Ω is the remaining part of the three dimensional space, $R^3\backslash\Omega$, and the binomial coefficient is added to take into account that electron cannot be distinguished. A maximal probability domain, MPD, is a region of space maximizing $p_\nu(\Omega)$. It will be denoted by Ω_ν.

The computation of p_ν (Equation (1)) is less difficult as it may seem, at least for certain forms of the wave function. In particular, for a single Slater determinant, as it is produced by Hartree–Fock, or Kohn–Sham calculations, one first computes the overlaps of all occupied orbitals over the regions Ω,

$$S_{ij}(\Omega) = \int_\Omega \phi_i(x)\phi_j(x)dx \quad (2)$$

Next, the eigenvalues of the matrix with elements S_{ij} are obtained (Equation (2)). From them, the probabilities are quickly computed for all ν with a recursive formula.[3] To obtain the MPDs, the presently running programs use a grid of small cubes, over which the S_{ij} are obtained analytically. A collection of such small cubes defines a domain Ω. Next, small cubes are added or deleted, modifying Ω to maximize a chosen p_ν.[4] An alternative optimization technique used triangulates the surface of Ω. The so-called "shape derivative" is computed on this surface, and the triangles are moved to increase p_ν.

Hartree–Fock wave functions for the crystals have been obtained using a modified version of the program Crystal.[5,6] A

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new program was written to produce the MPDs which were plotted using the program Xcrysden.[7]

Programs are now available to obtain MPDs for molecules, too, e.g., from the Gaussian program package.[8] MPDs can be produced also with correlated wave functions, via a Quantum Monte Carlo program, cf.[9,10] Presently, this implementation works only for molecules, but the same techniques could be applied to solids, too, e.g., by using the Casino program.[11] Probabilities can be computed for multi-determinant wave functions (see, for example[12]), but the optimization of Ω is not implemented yet.

The MPDs are close to ELF basins.[13] For single Slater determinants, in the ideal limiting case of strictly localized (non-overlapping) orbitals, the localization domain of the orbitals, the ELF basins and the MPDs become identical.[14]

We will also look at the populations, by integrating the electron density over regions of space, either given by MPDs or by ELF basins.

Results

We can divide space with Wigner–Seitz (Voronoi) cells,[15] using the midpoints between the nearest neighbor atoms as centers. Such a cell is shown on Figure 1. It corresponds to one of the ELF basins when only valence electrons are taken into account (in a pseudopotential calculation), and, within our numerical accuracy, it corresponds to the MPD for a pair of electrons, Ω_2 (from the same calculation). The probability to find two electrons in it is between 0.4 and 0.5 (cf. Table 1). Although this value may seem low, one has to keep in mind that the probability to find two out of eight independent particles cannot be larger than 0.312.
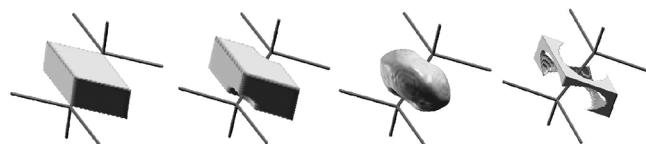

Figure 1. Domains corresponding to one of the bonds. From left to right: Wigner–Seitz (Voronoi) cell, ELF valence basin (all-electron calculation), MPD for a pair of electrons, (all-electron calculation), and the domain present in the ELF basin, not present in the MPD.

Table 1. Probabilities to find two electrons in a region of space attributed to the bonds, as defined by ELF basins and by MPDs.

| Element | Valence only Voronoi cell | All-Electron | |
		ELF	MPD
C	0.42	0.40	0.40
Si	0.45	0.43	0.43
Ge	0.43	0.36	0.37
Sn	0.43	0.36	0.36

Of course, there is a finite probability to find less or to find more than two particles in the cell. The distribution of probabilities is shown in Figure 2, and although it is a discrete distri-

bution, a fit by a Gaussian function passing through the points works well (as was assumed by *Fulde* and co-workers[16,17]).
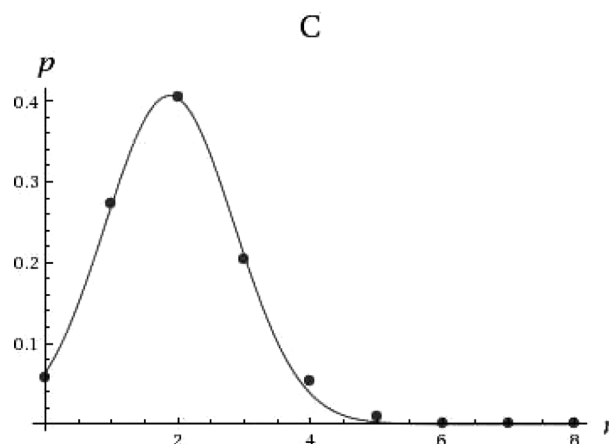

Figure 2. Discrete probability distribution for the diamond bond maximum probability domain and a Gaussian fit to it.

It was noticed[18] that the values of ELF are sensitive to the use of pseudopotentials. The penetration of core orbitals into the valence region significantly lowers ELF. However, the probabilities are only slightly reduced in all-electron calculations (cf. Table 1). The effect is more pronounced for germanium and tin, and slightly more important for ELF basins than for MPDs. The origin of this reduction comes from the penetration of the cores into the valence region, which is more important for the heavier elements.

One can notice that the change in the populations is smaller than one per cent (which corresponds to our numerical accuracy), when MPDs are considered, but more significant for ELF basins. This can be also seen in the core populations. The MPDs give numbers are within our numerical accuracy to those expected from the filling of the inner shells, whereas the ELF basins yield larger deviations, especially for germanium (28.0 for the MPD and 27.6 with ELF basins) and tin (46.1 for the MPD and 45.7 for the ELF basin). The deviation of the population of ELF basins was already noticed before.[19] One may ask why probabilities are less sensitive than populations. If we consider the difference between them and ELF basins to be of first order, so are the populations. The difference between the probabilities will be, however, only in second order, due to the variational nature of MPDs.

From the numbers given above for the cores, it is clear that the populations of the ELF basins for the bond regions in all-electron calculations are close to 2, and even more so for MPDs. The population of the Wigner–Seitz cells (and thus also that of the bonding regions in valence-only calculations) is equal to 2.

Interestingly, one can notice in Figure 1 that the MPD obtained in the all-electron calculation looks closer to what one would expect "chemically" for a bond region, but does not fill out the space, as does the ELF basin. The volume difference is not small, as can be seen in the last panel of Figure 1. We do not know at the present stage whether this 'shrinking' of

the domain is real, or just an artifact of our limited numerical accuracy. Even if the latter applies, it would not have shown up if the contribution of the outer region would have been significant for the MPD. If we make the hypothesis that the real MPD looks closer to the ELF basin, it thus certainly is very easy to "compress" it to the domain shown in the Figure A systematic "compression" of MPDs was studied, and will be published elsewhere.[20] Of course, the existence of "compressible" regions might be associated with places where room can be made for other atoms.

Conclusions

The results presented in this paper show that the regions of space maximizing the probability to find a pair of electrons in them (Ω_2s), are, for C-Sn (diamond structure) close to the basins of ELF. In this simple structure, one can see also these regions as Wigner–Seitz cells on a lattice of points given by the centers of the bonds. Up to this point, there is no essential improvement over ELF and MPDs might be seen as an alternative way of understanding ELF. It turns out, however, that the core-valence separation works better for MPDs than for ELF basins. This is also in agreement with earlier atomic calculations,[21] and may become interesting for crystals containing transition metal elements, where this separation was worse than for main group elements.

There is also a conceptual advantage of MPDs over using basins (based upon ELF or other similar quantities). Whereas the function used for constructing the basin (e.g. ELF) may have a sound physical significance, its basin stays an *a posteriori* mathematical construction. For MPDs the physical definition is present from their definition.

We would like to notice also that MPDs have more flexibility than ELF, as the number of electrons and the number of domains defining it can be chosen by the user.

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