Non-nuclear Maxima of the Electron Density

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Simple arguments and quantum mechanical calculations are used to analyze the occurrence of non-nuclear maxima (NNMs) in the electron density of crystals and molecules. The recent controversy concerning the experimental detection of NNMs in Be and Si is thus clarified, and NNMs are shown to be a normal step in the evolution of chemical bonding of homonuclear groups as internuclear distances decrease.

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The electron density of molecules and crystals, $\rho(\vec{r})$, exhibits large maxima at the nuclear positions and decays roughly exponentially further off. This being the most significant feature of ρ, the possible occurrence of local maxima of ρ at non-nuclear positions (NNMs) on the experimentally determined densities of Si and Be has been surrounded by controversy. Several experiments have supported the existence of NNMs. Sakata and Sato [1] found them studying the electron density of Si with the maximum entropy method (MEM), and using the accurate structure factors obtained by Saka and Kato [2]. Iversen *et al.* [3] also reported NNMs in Be applying the MEM to structure factors obtained by Larsen and Hansen [4]. The same experimental data have been recently used by Jayatilaka [5] to reconstruct a crystalline wave function without NNMs. On the theoretical edge, de Vries, Briels, and Feil [6] proposed a smart numerical experiment to show that the MEM method could be responsible for the NNMs found by Iversen *et al.,* and that neither a weighted MEM nor their own density functional calculations supported the NNMs in Be or in Si. This picture was further criticized by Iversen [7] who further justified the Be NNMs by a detailed Monte Carlo analysis of their original data. Mei *et al.* [8], on the other hand, have predicted unequivocal NNMs in the *bcc* phases of metallic Li and Na, based on the Hartree-Fock (HF) densities calculated with the CRYSTAL program [9]. It could be argued that there is no conclusive experimental or theoretical evidence of NNMs in the solid state.

We show in this Letter that this apparent chaos may be rationalized if geometric coordinates are taken into account and allowed to vary. NNMs of the electron density turn out to be the rule, and not the exception, among homopolar interactions, though at the experimental or theoretical equilibrium geometries few systems may display them. The controversy is resolved using extremely simple models of the electron density behavior. It is well known that the topological features of electron densities are dominated by the nuclei [10], and that promolecule or procrystal approximations to them are generally very good ones. Self-consistent field (SCF) or HF densities introduce small differences, mainly in bonding regions, where

a perpendicular contraction of charge around the bond paths usually appears. Finally, electron correlations tend to counteract slightly the previous effect. A lot is to be learned from the straightforward analytical examination of promolecular densities.

Let us consider a homodiatomic molecule, A_2 (A-A'), with internuclear separation $r = 2a_2$, and promolecular density $\rho(\vec{x}) = \rho_A(|\vec{x} - \vec{x}_A|) + \rho_A(|\vec{x} - \vec{x}_{A'}|)$, where ρ_A is the *in vacuo* spherical atomic density of atom A. In this model, the second derivatives of the density at the internuclear midpoint are easily found to be $\rho_\parallel'' = 2\rho_A''(a_2)$, $\rho_\perp'' = 2\rho_A'(a_2)/a_2$. The midpoint is then a bond critical point [10] (two negative perpendicular curvatures and one positive curvature parallel to the bond path) if the second radial derivative of the atomic densities is positive, i.e., if the radial atomic density is monotonically convex. Though many attempts have been made to prove this sensible hypothesis, it has only been possible to show that $\rho(a_2)$ is necessarily convex for $a_2 \geq r_{HO}$, the Hoffmann-Ostenhof radius [11]. Actually, it is accepted today that the exact nonrelativistic atomic densities show at least one nonconvex region for atoms with $Z = 3$–6, 16–32, and 45–92. Esquivel *et al.* [12] have shown that both HF and highly correlated atomic densities predict very similar behaviors, and that the origin of nonconvexity lies in the bare nucleus Coulomb field. Nonconvex atoms give rise to NNMs if a_2 lies within the nonconvex regions. These a_2 values *need not necessarily coincide* with equilibrium geometries. Bersuker *et al.* have proposed [13] that NNMs may develop by electron-electron mediated coupling of the ground state to low-lying excited states. We see, however, that, even in the absence of Bersuker's mechanism, homonuclear solids and molecules can be expected to have NNMs in the appropriate range of internuclear distances.

Electron-nuclei and electron-electron interactions introduce limited, nondestructive effects on the promolecular densities, as previously stated. In our example, a decrease of parallel curvatures and an increase (in absolute value) of perpendicular ones is to be expected, and actually encountered, favoring NNMs even in monotonically convex atoms. We have found, in fact, that this effect generates

NNMs in all homodiatomics with $Z = 3-9$, 11, 14–18, at least. The reliability of promolecular derivatives to predict the regions of stability of NNMs is very good. Figure 1 shows the analytical values of $\rho_\parallel''$ for the second period atoms using the quasi-HF densities of Koga *et al.* [14]. It is clear that the minima of these derivatives are narrower, and occur at smaller distances as Z increases. At this promolecular level, Li_2, Be_2, B_2, and C_2 display NNM regions, and N_2, O_2, F_2, and Ne_2 do not. SCF and correlation effects induce a general decrease of the parallel curvature that may be considered almost saturated at the SCF level. In this way, well developed NNM regimes arise, exemplified by the case of N_2 shown in the inset. All calculations have been done with the GAMESS code [15], using valence triple-ζ basis sets with diffuse and $3d + 1f$ polarization functions at the HF level, and including full single and double excitations at the CISD (configuration interactions, singles and doubles) level. Results are largely unaffected by extending the basis sets and/or improving the electron correlation treatment. It is to be noticed that the actual *NNM stability windows* are wider and have deeper wells, slightly displaced towards smaller distances, as compared to the promolecular results.

The position of the promolecular minima of $\rho_\parallel''$ is a very good indicator of the location of a plausible NNM. This is clearly seen in Fig. 2, where we show NNM windows for diatomic molecules up to the third period. All nonconvex and almost all convex atoms show NNMs. No NNMs have been found for Ne_2, Mg_2, and Al_2 at any level of computation, and it is very likely that these molecules lack them. Figure 2 also shows that the position of the windows is a periodic property, dependent on Z, and, therefore, atomic in nature. Equilibrium molecular geometries and the position of the windows
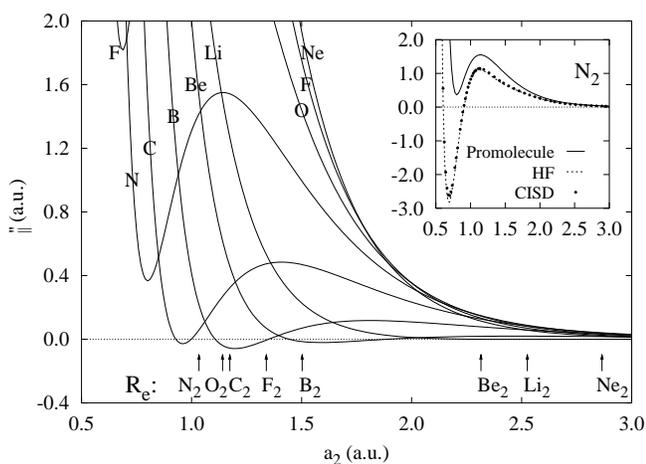
are decoupled, so that molecules at equilibrium in their ground states will bear only NNMs if their internuclear distances occur inside the stability windows. Much of the theoretical confusion that has dominated these issues is rooted in the nearness of some molecular geometries (particularly those of C_2, B_2, and P_2) to the upper edge of their respective windows. Slight variations in basis set quality, level of computation, etc., make the NNMs appear and disappear from paper to paper.

The mechanism of onset of NNMs has also been controversial. We have found two different ways by which a central bonding point becomes a NNM point as the internuclear distance decreases. The simplest mechanism appears in F_2, where the bond critical point just splits into a NNM and two new bond points. It is more complex in Li_2, where two points of null $\rho_\parallel''$ appear surrounding the initial bond point, and evolve first into a pair of NNMs plus three bond critical points, and then into a single NNM with two bond points, all along the internuclear line. This two-step mechanism, already occurring at the promolecular level, has been previously described by Cioslowski [16]. When the internuclear distance is further decreased, NNMs disappear by sudden recollapse, such as in F_2, or by more complex mechanisms, such as in C_2.

The problem of NNMs in heterodiatomics is now grasped easily. There are no symmetry fixed critical points along the internuclear axes anymore. At the promolecular level, critical points occur when $\rho_A'(r_c) = \rho_B'(r - r_c)$, where r_c is the position of the critical point measured from nucleus A, and r is the internuclear

FIG. 1. Promolecular $\rho_\parallel''$ derivatives calculated with the quasi-HF densities of Koga *et al.* [14]. a_2 is the distance from the nucleus. The experimental diatomic equilibrium semidistances are shown by arrows. Promolecular, molecular HF, and CISD $\rho_\parallel''$ values for N_2 are compared in the inset.
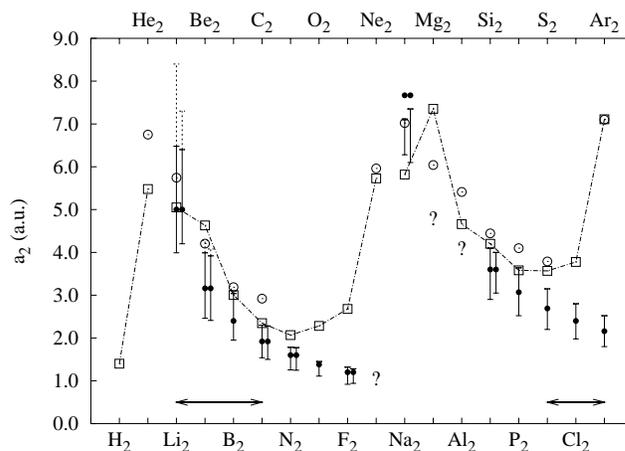
FIG. 2. Stability windows of NNMs in first, second, and third period homodiatomics. Full circles ($\bullet$) indicate the position of the minima of the valence promolecular $\rho_\parallel''$ value. Question marks indicate molecules lacking NNMs. Error bars point out for the NNM windows at the HF (left) and CISD (right, only for selected systems) levels for each system. Dotted bars correspond to regions with two internuclear NNMs. Open squares ($\square$) show the experimental equilibrium geometries of the diatomics, and open circles ($\odot$) the first neighbor distances in nonmolecular solids. The double arrows enclose those diatomics with NNMs at the promolecular level.

distance. This condition is independent of the one that assures a negative parallel curvature, $\rho_A''(r_c) + \rho_B''(r - r_c) < 0$, and thus a NNM. Given the narrow nonconvex regions of atoms, the simultaneous fulfillment of both conditions at a point r_c is most unlikely, independently of r. NNMs in diatomics should be exceptional, and we have actually been unable to find any in the 45 first and second period heterodiatomics we have examined.

Electron densities along internuclear lines in poly-atomics are completely dominated by the diatomic behavior, and the influence of the rest of the molecular environment tends to be perturbativelike. NNMs should be expected in homopolar bonds between identical atoms at the distances dictated by the homodiatomic analog, i.e., those in Fig. 2. This prediction has been fully supported by our calculations. For example, NNM windows have been found for C_2H_2, C_2H_4, C_6H_6, C_2H_6, Si_2H_6, and Si_8H_{18} that superimpose on those of the C_2 and Si_2 molecules. Since the C-C distances in acetylene, ethylene, and ethane are 2.23, 2.46, and 2.89 a.u., respectively, acetylene is the only one among these systems that could experimentally display a NNM at the C-C midpoint, though it is near the outermost stability edge. Small or not properly balanced computational basis sets have skipped it many times over the years.

In systems that contain homoatomic clusters, there is another interesting possibility, leading to *interstitial* NNMs. As the size of the cluster decreases, its central region suffers an unavoidable density accumulation that may eventually lead to the formation of a NNM. The promolecular model catches again the main features of this process. Let us consider an equilateral triangle (A_3) and a tetrahedron (A_4) of identical atoms as examples. Let also a_3 and a_4 be the distances of any atom to the center, respectively. At the baricenter of the triangle, the in-plane second derivatives of the density, ρ_{in}'', are degenerate by symmetry, and positive for large a_3 values. The perpendicular derivative is negative, and the baricenter is a second order saddle or ring critical point of ρ for those large a_3 values. In the A_4 case, all of the three second derivatives ρ'' are degenerate at the baricenter, and positive for large a_4 values, thus making the baricenter a local minimum or cage point. The promolecular derivatives are $\rho_{in}'' = \frac{3}{2}[\rho_A''(a_3) + \rho_A'(a_3)/a_3]$, $\rho'' = \frac{4}{3}[\rho_A'' + 2\rho_A'(a_4)/a_4]$. As ρ_A' is negative definite and ρ_A'' is bounded, there exists a threshold cluster size, for both the A_3 and A_4 configurations, such that smaller clusters necessarily accommodate an inner NNM. Notice that the appearance of this kind of NNM does not rely now on nonconvexity of atomic densities.

SCF effects will draw density from the ring or cage regions toward the interatomic lines, while electron correlation will oppose slightly to this concentration. The overall effect is a small delay in the onset of interstitial NNMs when the cluster shrinks as compared to promolecular results. We have found that the regions of stability

of central NNMs in A_3 and A_4 configurations are centered at cluster sizes with interatomic distances somewhat smaller than those found in the diatomic windows examined before. In systems with internuclear NNMs, such as Be, it is found that in the triangular configuration there first appear a couple of internuclear NNMs between every pair of Be atoms at almost exactly the appropriate Be-Be distance at which these NNMs appear in the diatomic ($a_3 = 2.36-2.45$ a.u.). Each of these pairs collapse to form a NNM at the center of each of the triangle's sides, also at the appropriate distance dictated by Fig. 2 ($a_3 = 2.14$ a.u.). On shrinking the cluster, a NNM at the triangle's center evolves ($a_3 = 1.92$ a.u.) that annihilates the peripheral ones ($a_3 = 1.63$ a.u.), surviving isolated until it also disappears ($a_3 = 1.04$ a.u.), leaving a ring point. In the Be_4 cluster, the above sequence is repeated for each triangular face on shrinking: first two NNMs per Be-Be pair that collapse, then a central NNM at the center of the tetrahedron, followed by the disappearance of the internuclear maxima. At $a_4 = 1.90$ a.u., and up to the smallest cluster geometries at which we have been able to obtain converged SCF results, a NNM appears at the center of the tetrahedron, first accompanied by the four maxima situated at the center of the faces, and alone from a particular threshold cluster size on. On the contrary, systems that most likely lack internuclear NNMs, such as Mg or Al, start developing interstitial maxima by an instability at the A_3 or A_4 center. Promolecular densities are again excellent predictors of the distances at which these phenomena are expected. Until now, we have not found exceptions to this behavior. Even hydrogen clusters, charged to avoid Janh-Teller distortions, show central NNMs. For example, H_4^{2+} has central maxima for H-H distances smaller than 3.12 a.u. (the experimental distance in H_2 is 1.40 a.u.). Central maxima also appear in H_3^+ for H-H distances smaller than 1.0 a.u. Promolecular densities predict this order cleanly.

There may also exist clusters particularly well suited to house central NNMs. This seems to be the case of the A_5 clusters in a trigonal bipyramid configuration. At the promolecular level, the two apical atoms may be understood as an A_2 molecule perpendicular to an A_3 cluster. At the center of the triangle, the negative perpendicular second derivatives introduced by the orthogonal A_2 molecule decrease the in-plane derivatives of the A_3 fragment, while the out-of-plane derivative is slightly increased. This greatly favors the transformation of the critical point at the triangle's center into a NNM. In fact, we have found that the Be_5 cluster accommodates central maxima for Be-Be distances in the triangular plane greater than 4.71 a.u., extending considerably the stability window shown in Fig. 2.

Homoatomic crystals behave locally like big clusters, subject to the same general principles we have presented. They will display interstitial NNMs if sufficiently compressed. Some of them, moreover, will present zero

pressure interatomic distances inside the stability windows of NNM, either internuclear or interstitial. Metallic lithium lies in the middle of the appropriate range. The calculations of Mei *et al.* [8] clearly showed interstitial NNMs. We have also used the CRYSTAL HF program [9] to examine the geometric behavior of its density. Though bounded by computational limits in the basis set size and quality, we think that our final densities are of reasonable quality. bcc Li develops two NNMs between each pair of first neighbor atoms at a lattice parameter $a = 8.22$ a.u., corresponding to a Li-Li distance of 7.12 a.u., in excellent agreement with the windows's edge in Fig. 2. On shrinking the lattice, the pair of NNMs fuse and end up in interstitial positions, generating a wealth of new topologies. Again, procrystalline densities predict exceedingly well the observed behavior. Unfortunately, solid Li is a very difficult system to deal with experimentally, and no attempt of a precise experimental determination of its electron density has been undertaken. Beryllium is at the very center of the controversy. Its equilibrium hcp Be-Be distances are 4.21 and 4.32 a.u., which lie just around the verge of the diatomic NNM window. It is to be noticed, however, that the hcp structure may be described as a set of vertex sharing trigonal bipyramids. As we have seen, the conditions for interstitial NNMs to appear in this type of clusters are particularly weak, and our previous arguments show that they should exist at those atom-atom distances. We have in fact found interstitial NNMs at the center of the bipyramids in our CRYSTAL calculations in metallic Be, in agreement with Iversen *et al.* [3]. It is extremely likely that they are actually there, though experiments must face a rather difficult problem in order to separate the NNMs from the background density: the density difference among the NNMs and the absolute minimum density point in the cell is smaller than 10^{-2} e/bohr^3. *Metallic NNMs are very shallow.* Alloys such as SbBe$_{13}$ and Be$_4$B show Be-Be distances smaller than hcp Be (4.033 and 3.972 bohrs, respectively) and are promising candidates to search experimentally for interstitial NNMs.

According to Fig. 2, boron is another interesting system. It is known in a large number of polymorphic forms, and is part of many alloys and intermetallic compounds with a big tendency to form boron clusters with sometimes extraordinary low B-B distances. Carbon, on the contrary, shows too large interatomic distances for NNMs to occur. However, its stability as a diamond phase with respect to pressure makes it a future candidate to investigate as soon as pressure technology gets above the TPa barrier. (Our estimation for an internuclear NNM to appear in carbon is found to be at $V/V_0 = 0.47$, or around TPa pressures with current equations of state [17].) Sodium is another solid with sure interstitial NNMs; hcp Mg is similar to hcp Be, and our CRYSTAL calculations also show NNMs at the center of trigonal bipyramids. fcc Al is too far from the internuclear window and does not have favoring bipyramids.

Silicon is again at the verge. Our best molecular computations (both in the diatomic and in the Si$_2$H$_6$ and Si$_8$H$_{18}$ clusters) do not show internuclear maxima at the diamond phase interatomic distances, $r = 4.444$ a.u., but our CRYSTAL calculation does. They are probably an artifact of the basis set, and we think that they are not actually present in the solid. Compression of silicon produces a large number of low symmetry phases with increasing coordination numbers but practically unchanged Si-Si distances [18]. These phases might well accommodate interstitial NNMs. Similar reasonings are applicable to other systems.

We conclude that the shell structure of atoms contained in promolecular densities is the basic organizing principle underlying the occurrence of NNMs. Rather than being an oddity, NNMs are a normal step in the chemical bonding of homonuclear groups, if analyzed in the appropriate range of internuclear distances. For most elements, however, this range occurs far away from the stable geometry under normal thermodynamic conditions. The experimental search of these objects may thus be guided through the most appropriate systems and geometries.

[1] M. Sakata and M. Sato, Acta Crystallogr. Sect. A **46**, 263 (1990).

[2] T. Saka and N. Kato, Acta Crystallogr. Sect. A **42**, 469 (1986).

[3] B. B. Iversen *et al.,* Acta Crystallogr. Sect. B **51**, 580 (1995).

[4] F. K. Larsen and N. K. Hansen, Acta Crystallogr. Sect. B **40**, 169 (1984).

[5] D. Jayatilaka, Phys. Rev. Lett. **80**, 798 (1998).

[6] R. Y. de Vries, W. J. Briels, and D. Feil, Phys. Rev. Lett. **77**, 1719 (1996).

[7] B. B. Iversen, J. L. Jensen, and J. Danielsen, Acta Crystallogr. Sect. A **53**, 376 (1997).

[8] C. Mei *et al.,* Int. J. Quantum Chem. **48**, 287 (1993).

[9] C. Pisani and R. Dovesi, Int. J. Quantum Chem. **17**, 501 (1980).

[10] R. F. W. Bader, *Atoms in Molecules* (Oxford University, New York, 1990).

[11] M. Hoffmann-Ostenhoff and T. Hoffmann-Ostenhof, Phys. Rev. A **16**, 1782 (1977).

[12] R. O. Esquivel *et al.,* Phys. Rev. A **47**, 936 (1993); R. O. Esquivel *et al.,* Phys. Rev. A **47**, 4735 (1993).

[13] G. I. Bersuker, C. Peng, and J. E. Boggs, J. Phys. Chem. **97**, 9323 (1993).

[14] T. Koga *et al.,* J. Chem. Phys. **103**, 3000 (1995).

[15] M. W. Schmidt *et al.,* J. Comput. Chem. **14**, 1347 (1993).

[16] J. Cioslowski, J. Phys. Chem. **94**, 5496 (1990).

[17] M. P. Grumbach and R. M. Martin, Phys. Rev. B **54**, 15 730 (1996).

[18] S. J. Duclos, J. K. Vohra, and A. L. Ruoff, Phys. Rev. B **41**, 12 021 (1990); B. G. Pfrommer *et al.,* Phys. Rev. B **56**, 6662 (1997).