Extension of Bright Wilson's Justification of the First Hohenberg Kohn Theorem to Non-Nuclear Maxima (NNM)

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In 2009, Mikael Johansson initiated a discussion on the "Computational Chemistry List" [1] questioning the applicability of Kato's cusp condition [2] and E. Bright Wilson's justification of density functional theory (DFT) [3] to "non-nuclear maxima" (NNM) also known as "non- nuclear attractors" (NNA) [4-10]. In almost every respect, a NNM behaves as a ghost atomic nucleus to which the gradient vector field of the electron density converge leading to the formation of well defined (pseudo)atomic well-defined basins as they are normally defined for atoms within Bader quantum theory of atoms in molecules (QTAIM) [11]. Within the point-like approximation of atomic nuclei, the wavefunction and the electron density exhibit cusps at the nuclear positions. As an attractor to the gradient vector field, the NNA is, however, indistinguishable form a a cusp even though the former is a true maximum and not a cusp [12,13]. E. B. Wilson has justified the first Hohenberg-Kohn first theorem [14] by arguing that since the integral of the electron density over all space yields the total number of electrons (N) which fixes the upper limit of summations that appear in the hamiltonian that involve N, and that since the density features cusps at the nuclei which fixes their positions and charge by virtue of Kato's cusp condition [15], the density contains all the necessary elements to fix the hamiltonian and hence all the electronic states and properties of the system. It will be shown that both Kato's condition and Wilson arguments can be extended to systems with NNMs [12,13]. The spherically-averaged derivative of the density with respect to *r* from any well-behaved point is strictly zero and since NNMs are not cusps but true maxima, this means that what we call the "*extended Kato's condition*" also applies to NNMs [12,13]. Numerical verifications will also be presented.

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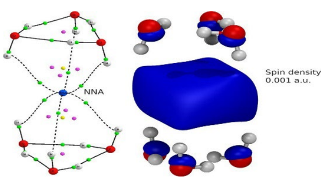

Figure 1

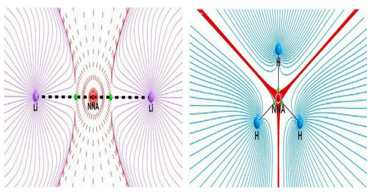

Figure 2

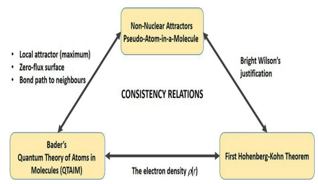

Figure 3