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A CONJECTURE ON THE CHANGE OF ELECTRONIC DENSITY OF A MOLECULE UNDER AN ISOTROPIC DILATATION OF THE NUCLEAR GEOMETRY

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Consider the lowest energy state of the electronic Hamiltonian in the Born–Oppenheimer approximation for one of the irreducible representations of the point symmetry group of a polyatomic molecule. Let N be the number of nuclei ($N \geq 3$) and assume Z_N to be the largest nuclear charge: $Z_N \geq Z_i$, $i \leq N-1$. Let $\boldsymbol{r}_0$ be a vector specifying the (internal) nuclear configuration of a molecule. It is convenient to regard $\boldsymbol{r}_0$ as the generator of an "isotropically independent" family of configurations, derived from $\boldsymbol{r}_0$ as $\boldsymbol{r}(a) = a\boldsymbol{r}_0$, with $a \geq 0$. Note that $a = 0$ corresponds to a configuration with all the nuclei collapsing into a point ("united atom" limit). The conjecture deals with the expectation values of the Coulombic operators Q_s:

$$Q_s = \sum_{i=1}^{n} ||\boldsymbol{R}_i - \boldsymbol{x}_s||^{-1}, \tag{1}$$

where $\boldsymbol{R}_i$ is the position vector of the ith electron (there are $n \geq 2$ of them), and $\boldsymbol{x}_s$ the position vector of the sth nucleus in 3-space. Operator Q_s represents the attractive interaction of all the electrons in the molecule with the nucleus s. The expectation value of this operator is $\langle Q_s \rangle_{r(a)}$, for a molecule with the nuclear configuration $\boldsymbol{r}(a)$ and in the electronic eigenstate mentioned above.

It is conjectured that if

$$\langle Q_N \rangle_{r(a)} \geq \langle Q_s \rangle_{r(a)}, \quad s \neq N, \tag{2}$$

then

$$\langle Q_N \rangle_{r(a)} = \langle Q_N \rangle_{r(a')} + A, \tag{3.1}$$

$$\langle Q_s \rangle_{r(a)} = \langle Q_s \rangle_{r(a')} + B, \tag{3.2}$$

with

$$A \leq B > 0 \quad \text{if } a < a'. \tag{3.3}$$

An equivalent expression is:

$$\langle Q_s \rangle_{r(a)} / \langle Q_N \rangle_{r(a)} \geq \langle Q_s \rangle_{r(a')} / \langle Q_N \rangle_{r(a')} . \tag{4}$$

In a qualitative sense, the result (3) means that the electronic density is *not* expected to decrease (under an isotropic dilatation of the geometry) to a greater extent about the nucleus with largest charge than about the nuclei with smaller charges. This conjecture is relevant to a number of results on convexity relationships of the electronic energy in configurational and abstract nuclear charge spaces, and to the calculation of upper and lower bounds to the energy [1–4]. Moreover, this conjecture, if valid, could provide an indirect proof of the "exploded molecule conjecture" [5], as discussed in ref. [1].

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