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Comment on ”Surface-charge distribution on a dielectric sphere due to an external point charge: examples of C_{60} and C_{240} fullerenes, Phys. Chem. Chem. Phys. 2013, 15, 20115”

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Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 200X
DOI: 10.1039/b000000x

Raggi, Stace, and Bichoutskaia[1] use Density Functional Theory (DFT) to calculate the surface charge distribution on a C_{60} molecule in the presence of an external point charge. They obtain partial atomic charges on the carbon atoms by means of the Mulliken population analysis method[2], which is known to give reliable information on the relative charge distribution while the absolute magnitude is sensitive to the basis set[3]. In addition, they use classical electrostatics to calculate[4,5] the surface charge distribution on a dielectric sphere due to an external point charge and compare the *relative* charge distribution with their DFT results[1]. They find good agreement when considering a dielectric sphere of radius a=3.8 Å and relative permittivity ε=3.45 for small and large distances, h, between the point charge and the center of the sphere/molecule. From these results they seem to suggest that a C_{60} molecule is best described as a dielectric sphere with ε=3.45 when it interacts with an external point charge[1].

However, by using their[1] Eq. (8) we find that the *relative* surface charge distribution only depends very weakly on ε for a given value of h. In the upper panel of Fig. 1, we show the *absolute* surface charge distributions for a single point charge outside spheres with radius 3.8 Å and ε=3.45, 7, 10, 20 or 1000. In the lower panel we show the same distributions but normalized such that their minimum values are set to -1. Our result for ε=3.45 is in perfect agreement with Ref.[1] but we also find that the relative charge distributions are nearly independent of ε (lower panel, Fig. 1).

We thus conclude that the relative surface charge distribution from classical electrostatics cannot be used to discriminate between different assumptions about the dielectric properties of fullerenes interacting with external charges. Calculations of interaction energies[6,7], however, are sensitive to ε. Comparisons with DFT results have unambiguously shown[7] that the interaction energies for a single point charge outside a C_{60} molecule is well described by assuming that the latter is a metallic sphere while an assumption of a low value of ε gives much less favourable results.

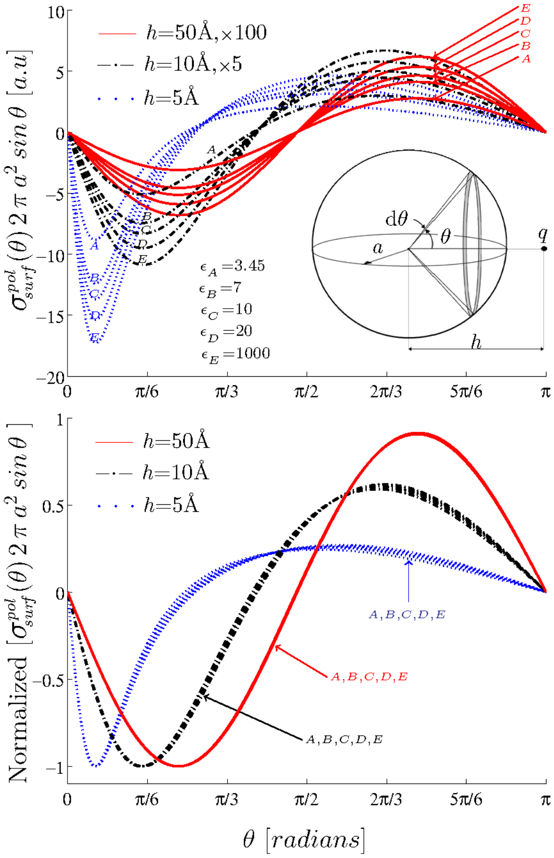

Fig. 1 Upper: Surface charge distributions - i.e. polarization surface charge densities multiplied by area elements $2\pi a^2 sin\,\theta$ - as functions of θ for a point charge q=15 a.u. at distances h=5, 10, and 50 Å from the center of a sphere of radius a=3.8 Å and relative permittivity ε=3.45, 7, 10, 20, or 1000. The h=10 and h=50 Å curves are multiplied by factors of 5 and 100, respectively. Lower: The corresponding normalized charge distributions (see text).

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