PHYSICAL REVIEW A **78**, 036102 (2008)

Comment on "Electron structure of a dipole-bound anion confined in a spherical box" and "Addendum to 'Electron structure of a dipole-bound anion confined in a spherical Box': The case of a finite dipole"

E. Ley-Koo[*]

Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, 01000 México, Distrito Federal,, México

(Received 9 May 2008; published 30 September 2008)

This Comment is motivated by some conceptual inconsistencies in the paper by Ronen [Phys. Rev. A **68**, 012106 (2003)] and its Addendum [S. Ronen, Phys. Rev. A **68**, 064101 (2003)]. While some of the inconsistencies are trivial—such as not distinguishing between anions and cations, and stating that polar molecules are made up of nuclei with positive and negative electric charges—the crucial one concerns the binding energy for an electron in a polar molecule, especially in the context of a confined molecular ion.

DOI: 10.1103/PhysRevA.78.036102   PACS number(s): 03.65.Ge, 31.10.+z, 31.70.−f, 31.70.Dk

The original paper [1] and its Addendum [2], commented herein, deal with the point-dipole and finite-dipole models of a polar molecule introduced in [3], with the new element of confinement of an electron to be bound, between concentric spheres and inside prolate spheroids, respectively. This Comment takes up the successive inconsistencies, each one with its proper weight.

References [4–6], corresponding to Refs. [24–25] in [1] and to Refs. [15–17] in [2], deal with the H_2^+ and HeH_2^+ molecular cations, not anions as cited in [1,2]. The statements about the nuclear charges and the distances of the electron from the nuclei appear in [2], immediately after citing Refs. [15–17] and in the paragraph introducing the prolate spheroidal coordinates, respectively. The finite dipole is defined by the position of the centers of positive and negative electric charges, associated with the distributions of nuclei and electrons, respectively. It should also be clear that the dipole moment modeling of a polar molecule is valid only asymptotically, and that the specific distribution of its nuclei dominates its structure at shorter distances.

The crucial part of this Comment is connected with the confinement in the models proposed in [1,2] and the general concept of binding energy. Therefore, it is important to discuss, successively and comparatively, the binding of an electron by a free polar molecule and by a confined polar molecule.

Specifically, the binding energy of an electron by a free polar molecule—characterized by its distribution of nuclei with charge numbers Z_i and positions $\vec{R}_i$, $i=1, 2, \ldots, N$ and the number of bound electrons $N_e=\Sigma_{i=1}^{N} Z_i$—is defined by the difference between the energies of the polar molecule and an electron at the ionization threshold minus the energy of the polar-molecule anion with the extra bound electron.

$$B(\vec{R}_i) = E_{pm+e}(\vec{R}_i) - E_{\text{anion}}(\vec{R}_i). \tag{1}$$

In general, the equilibrium positions of the nuclei in the respective systems must be different and the binding transition requires the analysis of the crossings of the respective energy hypersurfaces [7–9].

On the other hand, when a polar molecule is confined, the energies of the respective systems and the binding energy of the electron in the anion become functions of the confining parameters, p_c, the radii of the spheres, or the major axes of the spheroids,

$$B(\vec{R}_i, p_c) = E_{pm+e}(\vec{R}_i, p_c) - E_{\text{anion}}(\vec{R}_i, p_c). \tag{2}$$

Now, the analysis requires the crossings of the energy hypersurfaces including the additional dependence on the confining parameters.

In order to appreciate the basic inconsistency of what is presented in [1,2] in the light of the above equations for the binding energies, it is important to identify their implicit assumptions. For the binding by the free polar molecule, the first term in Eq. (1) is taken to be zero, i.e., $E_{pm+e}(\vec{R}_i)=0$. Similarly, for the binding by the confined polar molecule, in both [1,2] the corresponding choice is made in Eq. (2), i.e., $E_{pm+e}(\vec{R}_i, p_c)=0$, ignoring completely the effect of confinement, which is supposed to be the novelty of the proposed models and should be analyzed via the dependence on p_c. This is equivalent to taking $E_{pm+e}(\vec{R}_i, p_c \to \infty)=0$, for all values of p_c in Eq. (2) keeping the other term with its p_c dependence, thus basing the analysis in two different situations of confinement.

In conclusion, the choice of $E=0$ in [1,2] is inconsistent with the binding energy of Eq. (2), as spelled out in the preceding paragraphs. The interested readers are referred to [7–9] about the ionization of atoms confined inside spheres, in which the need to analyze the atoms and the products of their ionization as systems with the same components and the same interactions, including the same confinement conditions, is recognized to be crucial. The same must also be enforced in the analysis of the binding of an electron by a confined polar molecule.

This work was performed at Central China Normal University, Wuhan. The author thanks his hosts for their warm hospitality, especially Professor Yadong Yang and Professor Enke Wang for their academic support, Xiaofang Chen and Lijuan Zhou for scientific discussions, and to the library staff for technical assistance.

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[*] eleykoo@fisica.unam.mx

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