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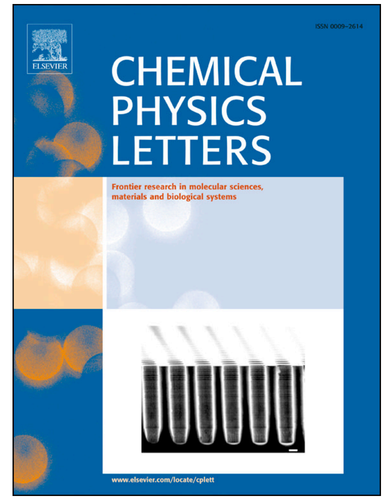

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Exact solution for the hydrogen atom confined by a dielectric continuum and the correct basis set to study many-electron atoms under similar confinements

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Abstract

The Schrödinger equation associated to the hydrogen atom confined by a dielectric continuum is solved exactly and suggests the appropriate basis set to be used when an atom is immersed in a dielectric continuum. Exact results show that this kind of confinement spread the electron density, which is confirmed through the Shannon entropy. The basis set suggested by the exact results is similar to Slater type orbitals and it was applied on two-electron atoms, where the H^- ion ejects one electron for moderate confinements for distances much larger than those commonly used to generate cavities in solvent models.

Keywords: Confined atoms, Dielectric continuum, Exact solution, Hartree-Fock, Basis set

1. Introduction

Confinement effects have been quite relevant for the study of many systems.[1, 2] In particular, such models are used to mimic the environment of atoms and molecules constrained spatially. On this line, for a long time solvent effects over electronic systems have been simulated by enclosing atoms or molecules within cavities of a dielectric continuum.[3, 4] From the beginning, this model was recognized as a confinement model by Jortner and Coulson,[5, 6] with an atom under the action of the potential

$$V(r) = -\frac{Z}{r} + V^{pol}(r), \tag{1}$$

where V^{pol} involves the polarization of the medium, which is related to the penetration of the wave-function (ψ) in the medium, evaluated as

$$Q(r_0) = \int_{r_0}^{\infty} dr r^2 |\psi(r)|^2. \tag{2}$$

In equations (1) and (2), Z represents the atomic number and r_0 the radius of a sphere, which defines the cavity of the confinement. Jortner and Coulson used the ground state wave-function of the hydrogen atom and this was used in the solution of the corresponding Schrödinger equation. Very recently, García et al. have reported strong arguments related to the asymptotic behavior involved with the wave-function when a dielectric continuum is present.[7, 8, 9] The main concerns of these authors are related to the basis sets used to represent Hartree-Fock or Kohn-Sham orbitals, because in principle, such basis sets have no information about the asymptotic behavior imposed by a dielectric continuum. Thus, they propose to use explicitly this information to build basis sets. Unfortunately, in their proposal these authors used functions related to the impenetrable confinement model,[10, 11, 12, 13] which is not appropriate in many cases.

The confinement considered in this article is related with the potential

$$\upsilon(\mathbf{r}) = \begin{cases} -\frac{Z}{r} \text{ for } r < r_0, \\ -\frac{Z}{\epsilon r} \text{ for } r \geq r_0, \end{cases} \tag{3}$$

where ϵ represents the relative permittivity. Naturally, this is not the potential defined by Jortner and Coulson since the polarization is not involved and consequently it gives only the confinement effects over the electronic structure. On this line, Ley-Koo and Rubinstein solved exactly the Schrödinger equation for the hydrogen atom confined by a constant potential (U_0),[14] which differs from equation 3 for $r > r_0$ with $\upsilon(r) = U_0$. For this case, the asymptotic behavior of the wave-function, ψ, has the form

$$\psi \approx r^{-l-1} e^{-\sqrt{-2\xi}r}, \tag{4}$$

where l is the quantum number related to the orbital angular moment and ξ is the energy of the system. From here, clearly the asymptotic behavior of a wave function immersed in a constant potential is not the same than that presented by Slater type orbitals(STO). This conclusion drove Rodriguez-Bautista et al. to build a new basis set for atoms confined by a constant potential[15] and they showed that basis sets with information related to the correct asymptotic behavior give better results than those basis sets designed for *free* atoms,[15, 16] which is in agreement with García.

From equation (3), it is clear that in the limit $\epsilon \to \infty$, we have a constant potential equal to zero from $r \geq r_0$, which suggests that a basis set build with similar functions to equation (4) are adequate to solve the Schrödinger equation associated

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