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Note on critical cage size for ionization of confined two-electron systems

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Abstract

The use of independent confinement models for the neutral and ionized two-electron atom or molecule to obtain the critical cage size for ionization is shown to be formally inconsistent. Instead, a treatment using the same Hamiltonian for the evolution of the ground state energy of the system is proposed, which allows for a consistent estimate of the first and second ionization energies as a function of cage size. Our calculations are based on the variational method applied to the helium atom confined by a spherical cage with impenetrable and penetrable confining walls.

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1. Introduction

The "atom in a box" model to study confinement effects on the ground-state energy of helium has been widely explored in the past considering either hard or soft spherical confinement walls [1–14]. Among this class of studies, the critical cage radius at which a confined many-electron atom undergoes ionization has been addressed by using Dirichlet-boundary adapted approaches such as numerical Hartree–Fock calculations [3,8] and density-functional theory [10], whereby the ionization radius is selfconsistently obtained.

More recently, for a helium atom confined by spherical rigid walls, a different approach to estimate the critical cage radius leading to first ionization, i.e. the transition $He \rightarrow He^+$, has been proposed [14]. This critical cage radius has been estimated by treating separately the He and the He^+ systems under the same confinement conditions. The ionization radius is then defined as that where the He and He^+ energies attain the same value, i.e. where the corresponding cage-size dependent energy curves cross (here we shall call this as the *superposition approach*). We note here that the same scheme had been applied before in the search of the ionization pressure for the hydrogen molecule leading to the transition $H_2 \rightarrow H_2^+$ using spheroidal impenetrable walls [15,16]. From our point of view this approach is formally inconsistent, since it deals with two independent systems not governed by the same Hamiltonian. To wit, while the neutral two-electron system is further confined until a cage size is found to produce an unbound electron (ionization), the system is still governed by the same Hamiltonian i.e. two electrons and nucleus (or nuclei in the case of H_2) provided no electron escapes from the confinement region.

The aim of this communication is to show that critical cage sizes for ionization should be consistently treated through the same Hamiltonian. Moreover, an heuristic argument is given to account for the cage-size evolution of the first and second ionization energies through a suitable partition of the Hamiltonian. An extension of these ideas is done for the case of confinement by penetrable spherical walls. Atomic units ($e = \hbar = m = a_0 = 1$) are used throughout unless otherwise indicated.

Let us first digress briefly on the concept of ionization for a free atom and then bring this idea within the context of a confined atom. A free atom is said to be ionized when one or more of its bound electrons acquire enough energy to jump into the continuum and hence become no longer bound to their parent

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nucleus. The threshold energy to extract one electron from its ground-state is known as the ionization potential. In the case of helium, for example, once the outermost electron is ionized (first ionization) we are left with the hydrogen-like He^+ ion whose ionization potential (second ionization) is immediately obtained from the corresponding hydrogen-like ground-state energy. This may be done so because the first electron has escaped the system. Accordingly, the first ionization potential may be known after deducting the second ionization potential from the total energy.

For the confined atom, however, the idea of ionization is not at first related to jump into continuum states but to states of positive energy appearing due to the confining potential. In this sense an ionized electron—while unbound to its parent nucleus—still remains within the confinement volume and interacts with the nucleus and the other electrons. For confining potentials of finite barrier height, a finite number of positive-energy states (including the ground-state energy, which is of our concern here) are allowed and the electrons may ultimately jump into the continuum leaving the system whereas for infinitely high barrier heights the unbound electrons will always remain trapped. Hence, the concept of ionization potential for a confined atom may be stated as the threshold energy required to produce an unbound electron. Clearly, while the electrons and nucleus remain in the same confinement volume, the same Hamiltonian governs the system with either ionized and/or bound electrons.

2. Method

For the sake of the subsequent discussion, let us consider a two-electron atom in its ground state and nuclear charge Z confined within a spherical cage of radius R with a confining barrier height V_0. The corresponding Hamiltonian is given as:

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + V(r_1, r_2) \tag{1}$$

with

$$V(r_1, r_2) = \begin{cases} -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} & (r_1, r_2 < R), \\ V_0(1) + V_0(2) & (r_1, r_2 \geqslant R). \end{cases} \tag{2}$$

The numerals 1 and 2 in Eqs. (1) and (2) refer to each electron, with r_1 and r_2 their corresponding radial positions relative to the origin and r_{12} the interelectronic distance. Also, in Eq. (2) we have made the explicit indication of the height of the potential barrier at the boundary felt by each electron, i.e. $V_0(1) = V_0(2) = V_0$.

For an infinitely high confining potential ($V_0 \to \infty$), we use the variational ansatz wavefunction proposed by Gimarc [2]:

$$\Psi(1,2) = N\Phi(1,2) f(r_1) f(r_2), \tag{3}$$

where $\Phi(1,2)$ is the free-system simply correlated function:

$$\Phi(1,2) = e^{-\alpha r_1} e^{-\beta r_2} + e^{-\beta r_1} e^{-\alpha r_2} \tag{4}$$

with α and β variational parameters and $f(r_i)$ cut-off functions such that the wavefunction vanishes at the boundary, defined as:

$$f(r_i) = (1 - r_i/R), \quad i = 1, 2, \tag{5}$$

and N a normalizing factor evaluated within the confined region.

In the case of a finite barrier height V_0—for simplicity of the treatment—the interior Ψ^i and exterior Ψ^e are chosen as the variational ansatz wavefunctions [7]:

$$\Psi^i(1,2) = A\phi_{1s}^i(r_1)\phi_{1s}^i(r_2) \quad (r_1, r_2 < R), \tag{6}$$

$$\Psi^e(1,2) = B\phi_{1s}^e(r_1)\phi_{1s}^e(r_2) \quad (r_1, r_2 \geqslant R) \tag{7}$$

where

$$\phi_{1s}^i(r_i) = e^{-\lambda r_i}(R - \gamma r_i), \tag{8}$$

$$\phi_{1s}^e(r_i) = e^{-\mu r_i}/r_i, \quad (i = 1, 2) \tag{9}$$

and λ, μ and γ variational parameters with A, B normalizing factors such that:

$$\int_{\Gamma_i} \left|\Psi^i(1,2)\right|^2 d\tau_1\, d\tau_2 + \int_{\Gamma_e} \left|\Psi^e(1,2)\right|^2 d\tau_1\, d\tau_2 = 1, \tag{10}$$

where Γ_i, Γ_e denote the interior and exterior domain of integration, respectively.

In either case, hard or soft walls, the energy functional associated to the Hamiltonian given by Eqs. (1) and (2) may be obtained through the relation:

$$E(\eta_1, \ldots, \eta_k; R, V_0) = \left\langle \Psi^i(1,2)\middle|\widehat{H}\middle|\Psi^i(1,2)\right\rangle_{\Gamma_i} + \left\langle \Psi^e(1,2)\middle|\widehat{H}\middle|\Psi^e(1,2)\right\rangle_{\Gamma_e} \tag{11}$$

whose minimization, for a given box radius R and barrier height V_0 renders the variational parameters $\eta_1, \ldots, \eta_k$.

Coming back to the case of the helium atom ($Z = 2$) and helium-like ions, we shall give now some heuristic arguments to study the evolution of the first and second ionization potential by a suitable partition of the total energy [Eq. (11)] which may be cast as:

$$E = E_{\mathrm{I}} + E_{\mathrm{II}}, \tag{12}$$

with E_{I} and E_{II} given as:

$$E_{\mathrm{I}} = \left\langle \Psi^i(1,2)\middle|H_2^i\middle|\Psi^i(1,2)\right\rangle_{\Gamma_i} + \left\langle \Psi^e(1,2)\middle|H_2^e\middle|\Psi^e(1,2)\right\rangle_{\Gamma_e} + \left\langle \Psi^i(1,2)\middle|\frac{1}{r_{12}}\middle|\Psi^i(1,2)\right\rangle_{\Gamma_i}, \tag{13}$$

$$E_{\mathrm{II}} = \left\langle \Psi^i(1,2)\middle|H_1^i\middle|\Psi^i(1,2)\right\rangle_{\Gamma_i} + \left\langle \Psi^e(1,2)\middle|H_1^e\middle|\Psi^e(1,2)\right\rangle_{\Gamma_e}, \tag{14}$$

and the following definitions have been made for the one-electron operators both for the interior and exterior regions:

$$\left.\begin{array}{ll} H_K^i = -\frac{1}{2}\nabla_K^2 - \frac{Z}{r_K} & (r_K < R) \\ H_K^e = -\frac{1}{2}\nabla_K^2 + V_0(K) & (r_K \geqslant R) \end{array}\right\}, \quad K = 1, 2. \tag{15}$$

This decomposition allows to identify E_{II} as the second ionization potential with reference to the free-atom case ($H_K^e = 0$, $\Gamma_i \to \infty$) and by virtue of Eq. (12) the first ionization potential is then identified as E_{I}. As we shall demonstrate further below, the above scheme allows to treat consistently the ionization of confined two-electron atoms using the same Hamiltonian.