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## LETTERS AND COMMENTS

# Comment on ‘The spectral decomposition of the helium atom two-electron configuration in terms of hydrogenic orbitals’

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## Abstract

Brief remarks are made concerning Hutchinson *et al*’s paper (2013 *Eur. J. Phys.* **34** 111) about the ground configuration of the helium atom and the importance of continuum states. The purpose of our comment is twofold: firstly, to indicate that even when using a good basis set, obtained using the self-consistent Hartree–Fock method, the contribution of other bound states and continuum ones is of some importance to calculate energy levels; and secondly, to emphasize that continuum states can be of great importance to satisfy several rigorous sum rules.

In paper [1] the authors considered the ground configuration of the helium (He) atom. Specifically, they discussed the contributions of other hydrogenic states to the ground state configuration  $1s^+1s^-$  and the importance of the continuum states in describing it correctly. In the language of theoretical atomic structure, the authors referred to *configuration interaction* (CI) concepts [2]. As the authors said, it is important to stress that most colleagues are shocked by the importance of the continuum hydrogenic states, and admit that the hydrogenic basis is a *poor basis set*, although they are sometimes the only ones at our disposal. It was attempted to show that even using good basis sets (Hartree–Fock wavefunctions, for example), CI methods are essential to explain many experimental results, especially for neutral or poorly ionized atoms.

With regard to the binding energy of the  $1s^+1s^-$  configuration, the interaction with discrete  $|1sns\rangle$  Hartree–Fock states

$$\Psi_{\text{ground}}^{\text{exact}} \approx a_1|1s^2\rangle + a_2|1s2s\rangle + \cdots + a_{15}|1s15s\rangle \quad (1)$$

depresses that energy in approximately  $1000 \text{ cm}^{-1}$  (about  $0.124 \text{ eV}$ ). Taking into account the continuum states

$$\Psi_{\text{ground}}^{\text{exact}} \approx a_1|1s^2\rangle + a_2|1s2s\rangle + \cdots + a_{15}|1s15s\rangle + \int dp a_p |\psi_p^{\text{cont}}\rangle \quad (2)$$

the binding energy gets depressed in approximately  $2000 \text{ cm}^{-1}$ . Therefore, for the ground state of He, the interaction with the continuum is as important as extensive discrete CI.

Beyond energy level numbers, we want to stress the importance of continuum states in the calculation of several related sum rules. One of them involves the (non-dimensional) *oscillator strength*<sup>1</sup>  $f_{ji}$ , a basic quantity in the study of the interaction between matter and radiation. Aside from the details, the intensity of a spectral line is proportional to  $f_{ji}$ . In fact, if the wavenumber  $\sigma_{ji} = (E_j - E_i)/hc$  is measured in  $\text{cm}^{-1}$  and  $N_j$  is the population of the highest level in  $\text{cm}^{-3}$ , then<sup>2</sup>  $I_{ji} = 0.667hc\sigma_{ji}^3 f_{ji} N_j \text{ erg cm}^{-3} \text{ s}^{-1}$ .

The most important sum rule is the Thomas–Reiche–Kuhn one for the sum of the oscillator strengths for *all* transitions which start from a definite state  $j$  of the atom: neglecting relativistic effects, for any  $N$ -electron system it is rigorously true that

$$\sum_i f_{ji} = N. \quad (3)$$

Although this rule was derived by classical arguments, it was used by Heisenberg to derive the commutation relations in his first paper on matrix mechanics. In equation (3) the summation must be carried out over *all* eigenstates of Hamiltonian, including continuum states. Therefore, the summation symbol is more properly represented by

$$\sum_i f_{ji} = \sum_i^{\text{discrete}} f_{ji} + \int_I^\infty \left( \frac{df}{dE} \right) dE = N, \quad (4)$$

where  $I$  is the atomic ionization energy.

Although it is not the purpose of this comment to expound the details of the calculation of the  $f_{ji}$  values, for which an extensive introduction to theoretical atomic physics is necessary, it is interesting to consider some cases. The simplest one is, of course, the H atom, where all calculations, for  $f_{ji}$  and  $(df/dE)$  can be carried out exactly [2, 3]. We give a few examples: for the  $1s$  state,  $\sum_{np}^{\text{discrete}} f(1s - np) = 0.565$ , therefore  $\int_I^\infty (df/dE) dE = 0.435$ . Similarly, for  $2s$  state the numbers are  $0.649$  (discrete) and  $0.351$  (continuum) whereas for  $3s$  state, we have  $0.707$  ( $d$ ) and  $0.293$  ( $c$ ) [3]. The contribution of the continuum is very important indeed.

For the He case (or more complex atoms), where exact analytical wavefunctions do not exist, we must resort to numerical calculations based on Hartree–Fock methodology [2]. Alkaline elements are particular cases, where analytical approximate radial wavefunctions can be expressed in terms of the effective quantum number  $n^* \equiv n - \delta$ ,  $n$  being the main quantum number and  $\delta$  the quantum defect, defined by  $(I - E_{nl})/Ry = Z_c^2/(n - \delta)^2$ . This concept gives origin to the quantum Defect theory developed by Seaton [4] among others.

Excited states, such as  $1snl$  can be described using successive  $\delta$  values. To describe the fundamental configuration  $1s^2$  we must use numerical values obtained with the Hartree–Fock methodology [2]. We have obtained

$$\sum_{np}^{\text{discrete}} f(1s^2 - 1snp) \cong 0.55, \quad (5)$$

<sup>1</sup> We speak of *emission* oscillator strength when  $E_j > E_i$ . Otherwise, it is an absorption one; the relation between them is  $g_i f_{ij} = -g_j f_{ji}$ .

<sup>2</sup> The coefficient  $0.667$  has the adequate dimensions so that  $[I_{ji}] = \text{erg cm}^{-3} \text{ s}^{-1}$ .

therefore, from equation 3  $\int_I^\infty (df/dE) dE \approx 1.45$  : the continuum contribution is very important for the  $1s^2$  state.

For excited states, as  $1snl$ , the calculations can be made using the quantum defect theory. Without considering details, we can use other sum rule, related to (3) . If

$$P_{nl,n'l'} = \int P_{nl}(r)P_{n'l'}(r)r dr, \quad (6)$$

it is true that for any atom having a single electron transition, the sum over *all* states  $n'l'$  including the  $\varepsilon l'$  continuum ones is

$$\sum_{n'l'} (P_{nl,n'l'})^2 = \overline{r_{nl}^2} = \int r^2 P_{nl}^2(r) dr. \quad (7)$$

When the concept of the quantum defect is valid to describe a state (1s2s case results, for example) in units of  $a_0^2 \approx 2.8 \times 10^{-21} \text{m}^2$

$$\overline{r_{nl}^2} \approx \frac{(n^*)^2}{2} [5(n^*)^2 + 1 - 3l(l+1)]. \quad (8)$$

Since  $n^* \approx 1.73$  for the state 1s2s,  $\overline{r_{2s}^2} \approx 23.66$ ; the Hartree–Fock method gives  $\overline{r_{2s}^2} \approx 23.60$  (a discrepancy of only  $2 \times 10^{-3}$ ). Carrying out the sum explicitly,  $\sum_{n'l'} (P_{nl,n'l'})^2 \approx 22.4$ ; the continuum contribution is small for the 1s2s state (about 5%).

In conclusion, even using good basis sets, such as the numerical ones provided by the Hartree–Fock method, continuum states are important for the calculation of energy levels, but more important for the fulfilment of the sum rules.

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