Excitations of H_2 by positron impact

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In this paper, we present a theoretical study of scattering cross sections for positron impact of electronic states of hydrogen molecule (H_2) using the scaling Born positron (SBP) approach. Cross sections to low-lying electronic states, $B^1\sum^+{}_u$, $C^1\Pi_u$, $B'^1\sum^+{}_u$, and $D^1\Pi_u$ are investigated. In an earlier theoretical effort [J.L.S.Lino, *Rev. Mex. Fis.* **62** (2016) 596], an application of the SBP approach for the $X^1\sum^+{}_g \rightarrow B^1\sum^+{}_u$ electronic excitation of the H_2 molecule, gave cross sections with reasonable qualitative agreement with experimental data [J.P. Sullivan *et al*., *Phys. Rev. Lett.* **87** (2001) 073201]. However, recent studies for the excitation of the $B^1\sum^+{}_u$ state by positron impact showed that this electronic state still demand of a refined degree of description of the quality of the cross sections (Weiss *et al*., *Eur. Phys. J.D* (2018) 72). The purpose of this work was to reexamine the $B^1\sum^+{}_u$ state and verify the quality of the numerical convergence of SBP method and extend the investigation to other states. The possibility to estimate a indirect contribution of multichannel effects (three states considering the ground X1, $B^1\sum^+{}_u$ and E, $F^1\sum^+{}_u$ state) are introduced within the SBP context. For the first time, integral cross sections to these new states using the SBP approach are reported. In the absence of the experimental data and theoretical developments, comparisons are made with analogous electron scattering.

Keywords: Born; positron; scaling.

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1. Introduction

Excitation of electronic states of molecules is important in several areas [1]. It is well known that an accurate theoretical study of description of positron collisions requires more than simply changing the sign of the projectile. For example, short-range polarization and correlation effects are different from electron scattering and the role of positronium channel (Ps) represent an special challenges (Ps channel is not present for electron case). The observation and absolute experimental data still represent a problem [2], same for targets as H_2 molecule. Specifically, for inelastic positron-H_2 scattering results (theoretical calculations and experimental) are modest when compared with inelastic electron-H_2 scattering. Sullivan *et al*. [3] produced experimental cross sections for the $B^1\sum^+{}_u$ state by positron impact and some reviews of a selection of measurements for H_2 can be found also in Surko *et al*. [4]. On the theoretical side, few calculations of cross sections for excitation of H_2 by positron impact have been reported. For example, Lino *et al.* [5] reported integral cross sections (ICS) for excitation of the $B^1\sum^+{}_u$ state using the Schwinger multichannel (SMC) method, Arretche *et al.* [6,7] reported the same $B^1\sum^+{}_u$ state using again the SMC method, and Lino [8,9] using the SBP approach reported cross sections for the $B^1\sum^+{}_u$ and $C^1\Pi_u$ states. With the advance of quantum mechanical computational methods, some very accurate *ab initio* calculations as the close-coupling, the R-matrix method, complex Kohn and Schwinger multichannel method were performed for positron scattering and these significant efforts were published by Surko *et al.* [4]. Many analytical formulas for positron-molecule scattering have been developed to overcome these difficulties (the merit of analytical expressions is of convenience and increased applicability when cross sections may be required in more complicated modeling situation). Kim [10] originally proposed an scaling plane wave Born (called BEf-scaling) to describe electron-molecule scattering and this method was adapted by Lino [8,9] to describe positron-molecule scattering (called SBP approach). Comparison with available theoretical calculations and experimental data showed that cross sections using the SBP approach to positron-molecule are encouraging [11-13]. Motivated by these results we have taken up the task to investigate the numerical stability of the SBP approach for H2 molecule. Here, we repeat the prior calculation of positron-H_2 scattering to $B^1\sum^+{}_u$ ($C^1\Pi_u$) state [9], and extend the investigation to $B'^1\sum^+{}_u$, and $D^1\Pi_u$ state. To the best of our knowledge there are no corresponding theoretical or experimental inelastic cross sections and in the absence of these results, comparisons are made with analogous electron scattering. A preliminary study using three-state of approximation to investigate the influence of open channels (energetically accessible electronic states multichannel effects) also is proposed.

In Sec. 2 we identify the SBP method for positron scattering. In Sec. 3 computational procedures and results are discussed. Conclusions are presented in Sec. 4.

2. Outline of theory

The SBP approach is given by

$$\sigma_{SBP} = (f_{\text{accur}}/f_{\text{Born}}) \cdot f(E) \cdot \sigma_{\text{Born}}, \tag{1}$$

where

$$f(E) = \left(\left[\frac{E}{E + (E_{\text{ps}} + E_{\text{exc}}} \right] \right), \tag{2}$$

where $E_{\rm ps}$ is the positronium energy, $E_{\rm exc}$ is the excitation energy, E is the energy incident positron particle, $f_{\rm accur}$ is an accurate dipole oscillator strength value from experiments or from accurate wavefunctions, and $f_{\rm Born}$ is the dipole oscillator strength value from first Born approximation (FBA). The first scaling proposed by Kim [10] for electron scattering replaces the "E" energy by $E + B + E_{\rm exc}$ where B is the ionization energy of the target electron. The original qualitative justification for this scaling was that the "effective" incident energy seen by the target electron is E plus the energy of the bound electron. The denominator Eq. (1) can seen as the scaling factor to represent the correlation between the positron and electron. We have used in Eq. (1)

$$E_{\rm ps} = B - 6.8 \ \ {\rm eV},$$

where 6.8 eV is the ground state binding energy of positronium. Cross sections for positron-impact and electron-impact excitation are identical when Born approximation is used but the relation $E_{\rm ps} = B - 6.8$ eV is used to identify the positron as incident particle. The Eq. (1) is only a indicator of the order of magnitude of a constant shift to be added to E and we have observed that studies using the SBP show equally good results for molecules. The FBA in Eq. (1) represent the starting point and is used in the scaling because the plane wave is the correct wave function at infinity for an particle with charge colliding with a target. As observed in Eq. (2), E is increased by a constant ($E_{\rm ps} + E_{\rm exc}$) and this modification has some consequences practical to the performance of the SBP method [8,9]. The $f(E)$ factor reduces the FBA at low energies while keeping the validity of the Born approximation at high energies and the SBP approach has the effect of correcting the FBA (the $f(E)$ factor also identify the positron as incident particle). The FBA can be written as

$$\begin{aligned} f^{FBA(\mathbf{k}_i,\mathbf{k}_f)} &= -(2\pi)^{-1} < S_{ki}|V|S_{kf} > \\ &= -(2\pi)^{-1} \int d^3\mathbf{r} e^{i(\mathbf{k}_i - \mathbf{k}_f)\cdot \mathbf{r}p} \\ &\times < \Phi_i|V|\Phi_f >, \end{aligned} \tag{3}$$

where V is the Coulombic interaction between the incident positron and the molecular target where Φ_i and Φ_f are initial and final electronic states of the target, respectively. Qualitatively, the FBA does not account distortion of plane wave in the vicinity of the target and is apply only to integrated excitation cross sections. When dealing with dipole transitions the long-range character of the dipolar coupling requires a larger number of partial waves and because of it, higher partial waves are not well described for several sophisticates *ab initio* methods [5]. This consideration is very important and we have observed that the SBP approach can provide realistic excitation cross sections for many targets, which are not only difficult to measure but also cannot easily be calculated with existing theories. The present study has several goals: first, as cited before to the best of our knowledge, no theoretical study using the SBP approach has been observed to $B'^1\sum^+{}_u$, $D^1\Pi_u$, and also E,$F^1\sum^+{}_u$ states. Second, in the present study we reexamine our previous calculations to $B^1\sum^+{}_u$, and $C^1\Pi_u$, states [9], and third, a study preliminary on a indirect multichannel effects (using E, $F^1\sum^+{}_u$ state) is discussed. As we will see, our results for positron-H_2 scattering are highly encouraging.

3. Computational procedures and results

Many articles have been published on positron-H_2 scattering using sophisticate basis set and here we have used the basis set presented in Table I (see Ref. [14]).

Whit this basis set in Table II we shows vertical excitation energies using the improved virtual orbital (IVO) [14].

Many theoretical papers were published on the generalized oscillator strengths (GOSs) for these transitions in H_2, from which integrated Born excitation cross sections can be derived. The integrated Born cross section $\sigma_{\rm Born}$ for the excitation of an atom or molecule in terms of the GOS is given by

$$\sigma_{\rm Born} = \left(\frac{4\pi a_0^2}{E/R}\right) \int_{Q_{\rm min}}^{Q_{\rm max}} G_{fi}(Q) d(\ln Q), \tag{4}$$

where R is the Rydberg energy and Q the momentum transfer and its minimum and maximum values. For a dipole and

TABLE I. Basis set used in H_2 (no contraction) [14].

		Exponent	Coefficient
H	s	33.644400	1.0
		5.055796	1.0
		1.146800	1.0
		0.321144	1.0
		0.101309	1.0
		0.030000	1.0
	P	1.114200	1.0
		0.259200	1.0
		0.060000	1.0
	d	4.5	1.0
		0.5	1.0
		0.25	1.0

TABLE II. Vertical excitation energies for H_2 molecule (eV).

H_2(state)	Eexc (eV)	Ref. [14]
$H_2(B^1\sum^+{}_u)$	12.10	8.51
$H_2(C^1\Pi_u)$	12.50	9.60
$H_2(B'^1\sum^+{}_u)$	14.14	14.14
$H_2(D^1\Pi_u)$	14.53	14.53
H_2(E,$F^1\sum^+{}_u$)	13.03	13.14

TABLE III. f_{acc} and f_{Born} values.

H2(state)	f_{acc}	f_{Born}
$H_2(B^1\sum^+{}_u)$	0.310	0.322
$H_2(C^1\Pi_u)$	0.355	0.348
$H_2(B'^1\sum^+{}_u)$	0.328	0.053
$H_2(D^1\Pi_u)$	0.086	0.095

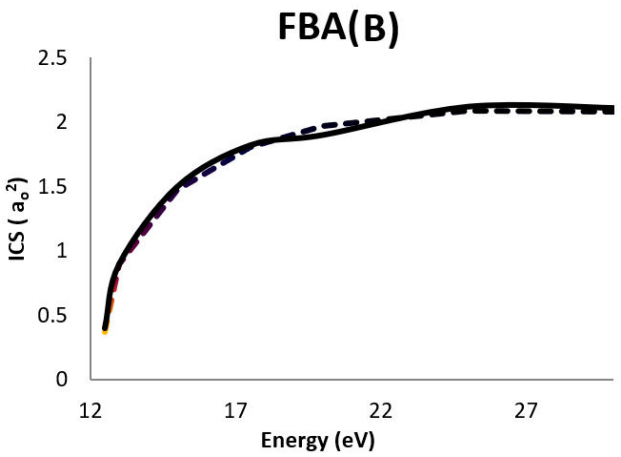

FIGURE 1. Integral cross sections (ICS) for positron-H_2 ($B^1\sum^+$, state) using FBA. Solid line, our FBA; dashed line, FBA [14].

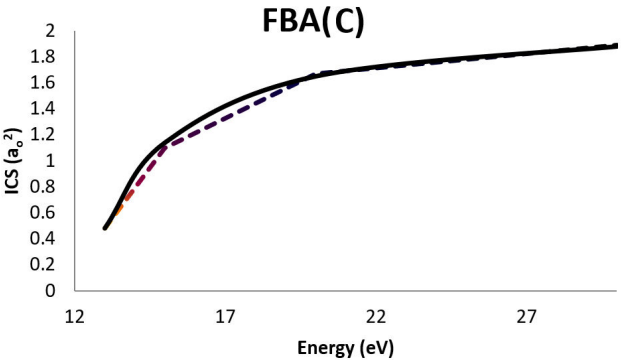

FIGURE 2. Same as Fig. 1. $C^1\sum^+$, state.

spin-allowed excitation, the GOS can be calculated using correlated wave functions fitted accurately [12]. With the fitted analytic function for the GOS, the integration of GOS in σ_{Born} can be carried out analytically for arbitrary "E". The appropriate f_{acc} and f_{Born} value to use in the SBP approach is given in the Table III (see Ref. [12]).

As a first step we will show results obtained using FBA for all states. These examples were chosen to allow assessment of the numerical quadrature technique using the FBA [5]. In Figs. 1-5 we show the FBA integral cross section for the $B^1\sum^+{}_u$, $C^1\Pi_u$, $B'^1\sum^+{}_u$, $D^1\Pi_u$, and E,$F^1\sum^+{}_u$ states compared with other FBA [14].

As observed in Figs. 1-5 our FBA results predicts equal cross sections with other FBA [14]. The results suggest a good convergence of cross sections in order to better describe

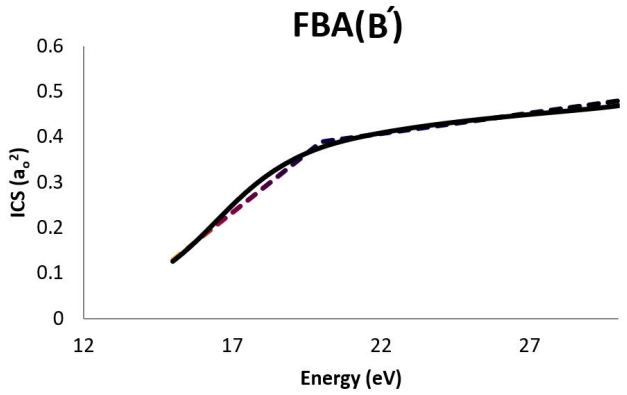

FIGURE 3. Same as figure 1. $B'^1\sum^+$, state.

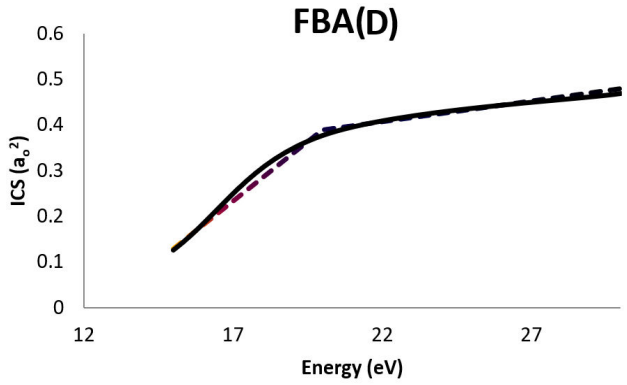

FIGURE 4. Same as Fig. 1. $D^1\Pi_u$, state.

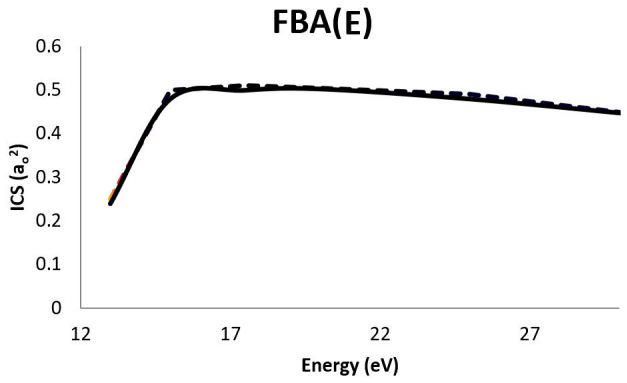

FIGURE 5. Same as Fig. 1. E,$^1F\sum^+{}_g$, state.

the SBP approach. When dealing with dipole allowed transition, such as $B^1\sum^+{}_g$, the long-range character of the dipolar coupling requires a larger number of partial waves and the SBP approach, in principle, can be used to include these contributions. In Fig. 6 we show the SBP method for 15, 20, 25, and 30 eV compared with the sophisticate ab initio SMC method [6], and experimental data [3]. As observed the SBP approach provides cross sections with the same order of magnitude as the experimental data [3] at low energy. Similarity (shape) between SBP approach and SMC method [6] also can

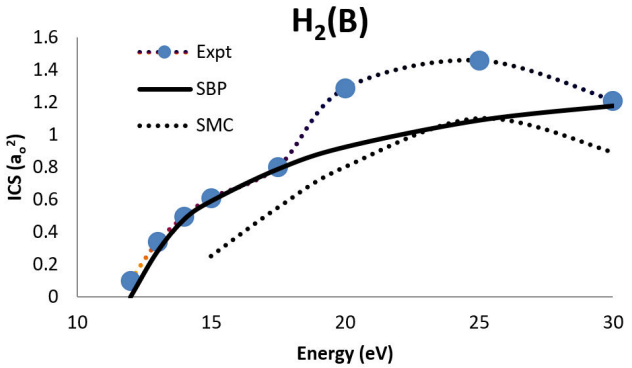

FIGURE 6. Integral cross sections for positron-H_2 ($B^1\sum^+{}_g$, state). Circle, experimental data[3]; solid line, SBP approach; dott line, SMC method [6].

TABLE IV. Integral cross sections positron-H_2 ($X^1\sum^+{}_g \rightarrow B^1\sum^+{}_g$) scattering (units a_o^2).

Energy (eV)	SBP	CCC[15]
13	0.33	0.25
20	0.93	1.30
25	1.10	1.50
30	1.20	1.55

TABLE V. Integral cross sections for positron-H_2 ($X^1\sum^+{}_g \rightarrow C^1\sum^+{}_g$) scattering (units a_o^2).

Energy (eV)	SBP	CCC [15]
15	0.20	0.20
20	0.70	1.73
30	1.05	1.10
40	1.15	1.20

be observed (as the SMC method is expected to produce better cross sections, the present SBP cross sections may be very encouraging).

As a next test to verify the stability of the $X^1\sum^+{}_g \rightarrow B^1\sum^+{}_g$ cross section, we have compared in Table IV the SBP method with the sophisticated convergence close coupling (CCC) for positron impact [15] at low energies (the comparison of our two-state ICS with CCC method shows that the SBP approach is encouraging).

As observed in Table II the agreement between our SBP and CCC [15] is reasonable, giving confidence that the SBP approach is promise (for positron scattering the CCC is expected to produce better cross sections [15]). In Table V we shows cross sections for the $C^1\Pi_u$ state using the SBP compared with CCC [15] method. Again the similar behavior between the two methods can be observed.

In Fig. 7 we shows cross sections for the $B'^1\sum^+{}_u$ state compared with the sophisticated *ab initio* SMC method [14]. As observed the SBP approach is similar with SMC method [14].

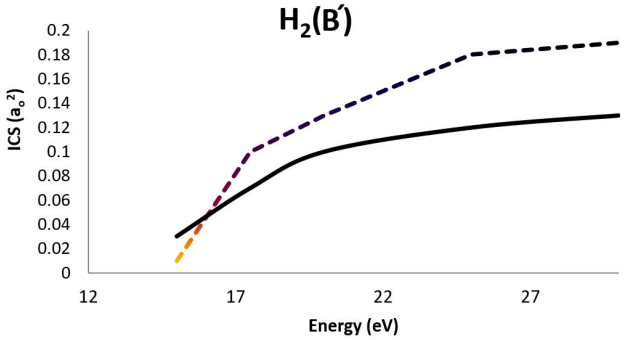

FIGURE 7. Integral cross sections for positron-H_2 ($B'^1\sum^+{}_g$, state). Solid line, SBP approach, dashed line, SMC method [14].

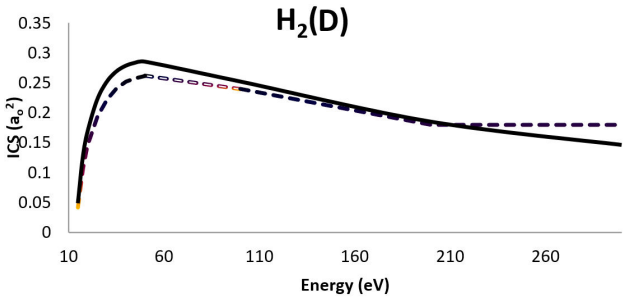

FIGURE 8. Integral cross sections for positron-H_2 ($D^1\sum^+{}_u$, state). Solid line, SBP approach, dashed line, BEf-scaling for electron [16].

In Fig. 8 we shows cross sections using the SBP approach for the $D^1\sum^+{}_u$ state compared now with the BEf-scaling for electron case [16]. As expected at high energies the cross sections by positron impact and electron impact tend to get closer.

As a possible criteria to verify again the stability of the $X^1\sum^+{}_g \rightarrow B^1\sum^+{}_g$ cross section, we have carried out calculations in three-state of approximation to investigate the influence of open channels (energetically accessible electronic states multichannel effects). Evidently, the FBA does not account multichannel effects and here we have used a alternative mechanism, *i.e.*, a indirect study to verify the contribution $(\sum \text{Born})_{n=\text{states}}$ and $(\sum E_{\text{exc}})$ in Eq. (1). The three states was done considering the ground X^1, B^1 and E states.

As knowledge is expected that the "E_1 state" as a open channel does not disturb the $X^1\sum^+{}_g \rightarrow B^1\sum^+{}_g$ cross section, which should not be a surprise [6]. We can easily see that the Fig. 9 satisfy this criterion, giving confidence that our preliminary study is consistent.

In the Table VI integral cross sections for the $B^1\sum^+{}_u$, $C^1\Pi_u$, $B'^1\sum^+{}_u$, and $D^1\Pi_u$ electronic state using SBP approach are listed for future reference (units a_o^2).

When positrons annihilate on many-electron molecules, the annihilation cross sections is traditionally written as [17-20]

$$\sigma_a = \sigma_{2\gamma} Z_{\text{eff}}, \tag{5}$$

TABLE VI. Integral cross sections for $B^1\sum^+{}_u$, $C^1\Pi_u$, $B'^1\sum^+{}_u$, and $D^1\Pi_u$ electronic state using SBP approach (a_o^2).

E(eV)	$B^1\sum^+{}_u$	$C^1\Pi_u$	$B'^1\sum^+{}_u$	$D^1\Pi_u$
12.5	0.2406	0.0	0.0	0.0
15	0.600	0.4750	0.0384	0.0488
17.5	0.8019	0.6934	0.0728	0.1247
20	0.9381	0.8450	0.0916	0.1678
25	1.1040	1.0407	0.1130	0.2212
30	1.1940	1.1516	0.1238	0.2515
35	1.2322	1.2136	0.1293	0.2691
40	1.2488	1.2457	0.1317	0.2788
45	1.2498	1.2506	0.1322	0.2840
50	1.2411	1.2603	0.1316	0.2858
60	1.2081	1.2414	0.1286	0.2836
70	1.1669	1.2081	0.1243	0.2608
80	1.1205	1.1693	0.1197	0.2550
90	1.0760	1.1288	0.1151	0.2537
100	1.0333	1.0889	0.1106	0.2525
150	0.8570	0.9162	0.0919	0.2132
200	0.7335	0.7892	0.0786	0.1851
250	0.6407	0.6944	0.0688	0.1631
300	0.5710	0.6213	0.0613	0.1462
400	0.4716	0.5159	0.0506	0.1212

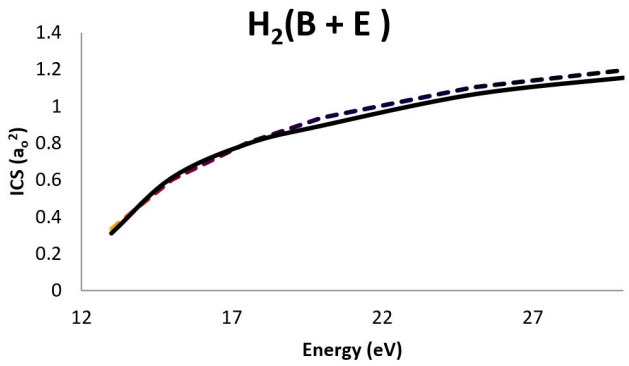

FIGURE 9. Integral cross sections for positron-H_2 using tree states. Dashed line, $X^1\sum^+{}_g \rightarrow B^1\sum^+{}_g$ using SBP approach. Solid line, $X^1\sum^+{}_g \rightarrow B^1\sum^+{}_g + E, {}^1F\sum^+{}_g$ states using SBP approach.

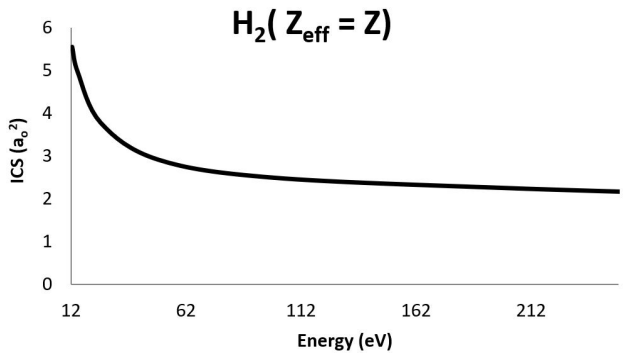

FIGURE 10. Z_{eff} using the SBP approach. Solid line, SBP approach.

where

$$Z_{\text{eff}} = \int \sum_{i=1}^{z} \delta(\mathbf{r} - \mathbf{r}_i) \times |\psi(\mathbf{r}_1, \ldots, \mathbf{r}_z\mathbf{r})|^2 d\mathbf{r}_1 \ldots d\mathbf{r}_z d\mathbf{r}, \quad (6)$$

is the effective number of electrons that contribute to the annihilation process, and $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_z\mathbf{r})$ is the total wave-function of the Z electron and one positron coordenates. If substitutes the asymptotic, plane wave function into Eq. (6), one obtains $Z_{\text{eff}} = Z$ (classical). We have noted that the SBP approach can determine the Z_{eff} classical based on the Born approximation, *i.e.*, the ${Z_{\text{eff}}}^{(\text{SBP})}$ represent also a important criteria to check the quality of SBP approach using the FBA. The accuracy of the Z_{eff} Born approximation can be given by

$${Z_{\text{eff}}}^{(\text{SBP})} = [(\sigma_{\text{Born}}/\sigma_{\text{SBP}})]Z. \quad (7)$$

In Fig. 10, we present ${Z_{\text{eff}}}^{(\text{SBP})}$ for the H_2 using, for example, $B^1\sum^+{}_g$ state. As observed the Z_{eff} shows aspects of convergence with Z classical ($Z = 2$) and indicate that the SBP approach is significant and suggested that Eq. (7) can be used as a strategies to treat convergence characteristic of the SBP approach.

4. Conclusion

Electronic excitation by positron impact is very challenging for theoreticians and experimentalists and as observed in our study inelastic cross sections for $e^+ - H_2$ scattering still are scarce. Analysis of the results indicated that electronic excitation of H_2 by positron impact using the SBP approach illustrate good convergence characteristics of the procedure when compared with *ab initio* method at low energies for the $B^1\sum^+{}_u$ state. A second observation is that the $B^1\sum^+{}_u$, and $C^1\pi$ cross sections are practically equal and these results can motive experiments. In the absence of experimental or theoretical data for $C^1\pi$, and $D^1\sum^+$ electronic states the SBP approach was compared with electron scattering case and for energies lower the cross sections for electrons being smaller in magnitude compared with positron scattering (this is expected). A preliminary study on effects multichannel showed that a indirect description multichannel can be improved to estimate cross sections, as for example the presence of the $E,F^1\sum^+{}_g$ state as an indirect open channel not disturb the $X^1\sum^+{}_g \rightarrow B^1\sum^+{}_g$ cross section, which is not surprise but the test using the SBP approach is specially relevant. Finally, the SBP approach for positron-H_2 suggests that the method is economical in the sense that relatively small basis set are capable of providing reliable cross sections with small effort computational. We also conclude that Z classical parameter is consistently good, giving confidence that the SBP method is significant for investigate positron-H_2 scattering. We believe that the cross sections using the SBP method may stimulate other experimental measurements be done to confirm our studies.

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