

## $Z_{\text{eff}}$ according to the Schwinger multichannel method in positron scattering

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We use the wave function from the Schwinger multichannel method to calculate  $Z_{\text{eff}}$ —an annihilation parameter of positron-atom (or molecule) scattering. These  $Z_{\text{eff}}$  are evaluated from the  $(N+1)$ -particle wave function and are calculated in a fully *ab initio* way (in a quantum chemistry sense). Our first applications are for positron scattering against He atoms and  $\text{H}_2$  molecules. Our results for both systems are in excellent agreement with experimental data at thermal energies.

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### I. INTRODUCTION

Annihilation rates of positronium in molecular environments have been recently measured (see Table I) and shown to be much larger than expected [1]. These experiments at room temperature have given annihilation parameters  $Z_{\text{eff}}$  sometimes several orders of magnitude larger than the classical expected values (about the size of the number of electrons involved in the process). No theoretical calculation has confirmed the experimental data up to now. The theoretical task is extremely difficult since it may require an approach that keeps the many-body character of the wave function.

Recently, Germano and Lima [4] have adapted the Schwinger multichannel method (SMC) [5] for low-energy positron-molecule scattering. The method is fully *ab initio* in a quantum chemistry sense: for complete convergence it depends only on the Cartesian Gaussian basis-set size and on how close to complete we are able to computa-

tionally construct a configuration-interaction space from this basis set. In this paper, we present the theoretical procedure for calculating the parameter  $Z_{\text{eff}}$  according to the SMC. As first applications we present very promising results for simple electronic-structure systems as  $e^+$ -He and  $e^+$ - $\text{H}_2$ .

### II. THEORY

The dimensionless parameter  $Z_{\text{eff}}$  is related to the annihilation rate  $\Gamma$  by the expression

$$Z_{\text{eff}} = \Gamma(\pi r_0^2 cn)^{-1}, \quad (1)$$

where  $n$  is the density of atoms or molecules,  $r_0$  is the classical radius of the electron, and  $c$  is the speed of light.  $Z_{\text{eff}}$  is the number of effective electrons that participate in the annihilation process when the target is scattered by a positron. It is given by [6]

$$Z_{\text{eff}}(\mathbf{k}_i) = \sum_{j=1}^N \langle \Psi_{\mathbf{k}_i}^{(+)}(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{r}_p) | \delta(\mathbf{r}_j - \mathbf{r}_p) | \Psi_{\mathbf{k}_i}^{(+)}(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{r}_p) \rangle, \quad (2)$$

where  $N$  is the total number of electrons of the target,  $\mathbf{k}_i$  is the direction of the incoming positron,  $\mathbf{r}_j$  are electron coordinates,  $\mathbf{r}_p$  is the positron coordinate, and  $\Psi_{\mathbf{k}_i}^{(+)}(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{r}_p)$  is the total  $(N+1)$ -particle wave function of the system.

The bilinear variational expression for the scattering amplitude is [4]

$$[f(\mathbf{k}_f, \mathbf{k}_i)] = -\frac{1}{2\pi} \left[ \langle S_{\mathbf{k}_f} | V | \Psi_{\mathbf{k}_i}^{(+)} \rangle + \langle \Psi_{\mathbf{k}_f}^{(-)} | V | S_{\mathbf{k}_i} \rangle - \langle \Psi_{\mathbf{k}_f}^{(-)} | A^{(+)} | \Psi_{\mathbf{k}_i}^{(+)} \rangle \right], \quad (3)$$

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TABLE I. Measured values of  $Z_{\text{eff}}$  (thermal energies).

Molecule	Formula	$Z$	$Z_{\text{eff}}$	Our results
Helium	He	2	3.94 <sup>a</sup>	4.20
Hydrogen	$\text{H}_2$	2	14.7 <sup>b</sup>	13.63
Methane	$\text{CH}_4$	10	140 <sup>b</sup>	
Butane	$\text{C}_4\text{H}_{10}$	34	15 000 <sup>b</sup>	
Benzene	$\text{C}_6\text{H}_6$	42	18 400 <sup>c</sup>	

<sup>a</sup>Reference [2].

<sup>b</sup>Reference [3].

<sup>c</sup>Reference [1].

where

$$A^{(\pm)} = Q\hat{H}Q + PVP - VG_p^{(\pm)}V. \quad (4)$$

Expansion of the trial scattering wave functions in the form

$$|\Psi_{\mathbf{k}}^{(\pm)}\rangle = \sum_m a_m^{(\pm)}(\mathbf{k}) |\chi_m\rangle, \quad (5)$$

and a stationary condition for  $[f(\mathbf{k}_f, \mathbf{k}_i)]$  with respect to the coefficients  $a_m^{(\pm)}(\mathbf{k})$  lead to

$$a_m^{(+)}(\mathbf{k}_i) = \sum_{m'} (d^{-1})_{mm'} \langle \chi_{m'} | V | S_{\mathbf{k}_i} \rangle \quad (6)$$

and a similar equation for the coefficients  $a_n^{(-)}(\mathbf{k}_f)$ . Insertion of expression (6) back into Eq. (5) gives straightforwardly our working equation for the  $(N+1)$ -particle scattering wave function

$$|\Psi_{\mathbf{k}_i}^{(+)}\rangle = \sum_{m,m'} |\chi_m\rangle (d^{-1})_{mm'} \langle \chi_{m'} | V | S_{\mathbf{k}_i} \rangle, \quad (7)$$

where

$$d_{mn} = \langle \chi_m | A^{(+)} | \chi_n \rangle. \quad (8)$$

If now we insert Eq. (7) (and a similar equation for  $|\Psi_{\mathbf{k}_f}^{(-)}\rangle$ ) into Eq. (3), we find our usual expression for the scattering amplitude [4]

$$[f(\mathbf{k}_f, \mathbf{k}_i)] = -\frac{1}{2\pi} \left[ \sum_{m,n} \langle S_{\mathbf{k}_f} | V | \chi_m \rangle (d^{-1})_{mn} \langle \chi_n | V | S_{\mathbf{k}_i} \rangle \right]. \quad (9)$$

If we use the definition of  $|\Psi_{\mathbf{k}_i}^{(+)}\rangle$  given by Eq. (7) in the expression of  $Z_{\text{eff}}$  [Eq. (2)], we obtain

$$Z_{\text{eff}}(\mathbf{k}_i) = \sum_{j=1}^N \sum_{m,n,m',n'} \langle \chi_{n'} | V | S_{\mathbf{k}_i} \rangle \langle S_{\mathbf{k}_i} | V | \chi_{m'} \rangle (d^{-1})_{mm'}^* (d^{-1})_{nn'} \langle \chi_m | \delta(\mathbf{r}_j - \mathbf{r}_p) | \chi_n \rangle. \quad (10)$$

It is very important to observe that the definition of the wave function, as given in Eq. (7), is valid only in regions where the potential is nonzero (this comes from a property of the Schwinger variational method). Note, however, that the presence of Dirac's  $\delta$  function in Eq. (2) implies that the integral will contribute to  $Z_{\text{eff}}$  only when the positron and the electron have a probability different from zero of occupying the same position. Since the electrons of the target are always in the region where the potential is not null, the use of expression (7) is allowed.

Usually the available experimental values for  $Z_{\text{eff}}$  are angular unresolved. Thus for direct comparisons we must average the theoretical parameter over all possible orientations of  $\mathbf{k}_i$ , i.e.,

$$\bar{Z}_{\text{eff}} = \frac{\int d\Omega_{\mathbf{k}_i} Z_{\text{eff}}(\mathbf{k}_i)}{\int d\Omega_{\mathbf{k}_i}}, \quad (11)$$

where  $d\Omega_{\mathbf{k}_i}$  is the solid angle.

After straight manipulation, we have

$$\bar{Z}_{\text{eff}} = \frac{1}{4\pi} \text{Tr} \left[ \underline{d}^{(-1)} \underline{S} \underline{d}^{(-1)\dagger} \underline{Z} \right], \quad (12)$$

where the matrix elements are

$$S_{mn}(k_i) = \int d\Omega_{\mathbf{k}_i} \langle \chi_m | V | S_{\mathbf{k}_i} \rangle \langle S_{\mathbf{k}_i} | V | \chi_n \rangle, \quad (13)$$

$$Z_{mn} = \sum_{j=1}^N \langle \chi_m | \delta(\mathbf{r}_j - \mathbf{r}_p) | \chi_n \rangle, \quad (14)$$

and  $d_{mn}$  are defined as in Eq. (8).

All matrix elements of expression (12) can be obtained from our earlier computer codes [4] except  $Z_{mn}$ . These matrix elements are combinations of overlap integrals in-

volving four Cartesian Gaussian functions

$$\int d^3r g_1(\mathbf{r})g_2(\mathbf{r})g_3(\mathbf{r})g_4(\mathbf{r}), \quad (15)$$

where each Cartesian Gaussian function has the form

$$g_i(\mathbf{A}, \alpha; \mathbf{r}) = N_{lmn} (x - A_x)^l (y - A_y)^m (z - A_z)^n \times \exp \left\{ -\alpha [(x - A_x)^2 + (y - A_y)^2 + (z - A_z)^2] \right\}. \quad (16)$$

The use of Cartesian Gaussian functions in the expansion of the total wave function makes the calculation of these overlap integrals [Eq. (15)] very simple (although cumbersome).

More details about the SMC method and how polarization effects are treated (including the construction of the configuration space) can be found in Ref. [4]. In what follows we present a first application of the expressions (10) and (11) for  $e^+$ -He and  $e^+$ -H<sub>2</sub> scattering.

### III. RESULTS FOR He

The SCF wave function for the ground state of the He atom was obtained with a [10s] Cartesian Gaussian basis [7], resulting in a electronic energy of  $-2.86167$  hartrees. We have used 58 Cartesian Gaussian basis functions for the SMC calculations. In addition to the SCF basis we have included six  $p$  functions at the He center (with exponents 15.0, 5.0, 1.5, 0.5, 0.16, and 0.03) and one  $p$  function (exponent 0.5) on each corner of a cube centered at the He atom. These functions were included to account for polarization effects. The cube was used

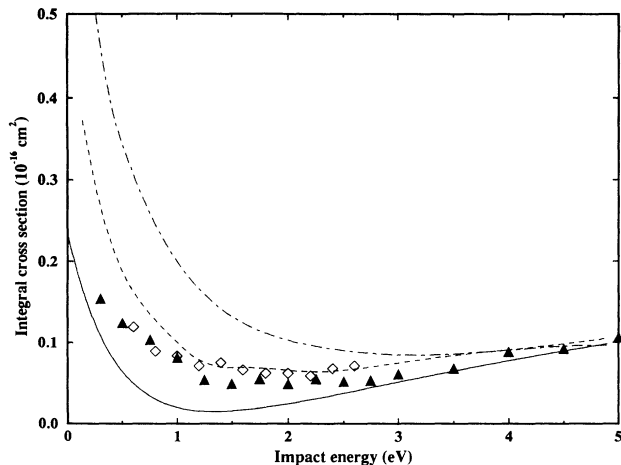


FIG. 1. Elastic integral cross sections for  $e^+$ -He scattering at low energies. Experimental points: diamond, Mizogawa *et al.* [8]; triangle, Stein *et al.* [9]. Theoretical curves: solid line, present (SP) results; dot-dashed line, results of McEachran *et al.* [10]; dashed line, results of Campeanu and Humberston [11].

to couple higher partial waves than those obtained with  $s$  and  $p$  functions at a single center. We also added one  $s$  function (exponent 0.1) centered on each face center of the cube. The distance from the He center to the face of the cube was taken to be  $1a_0$ . To construct the closed-channel space we used all possible single-particle excitations to a set of simple virtual orbitals made with the same SCF basis plus the additional functions. We included all symmetries, summing up 3364 configurations. Our  $Z_{\text{eff}}$  is calculated for positron impact energy ranging from 0.001 to 4.9 eV. We took 11 different trial bases (corresponding to different cube sizes and different exponents of Gaussian functions on the cube corner and on the face center of the cubes) and found small differences for the parameter  $Z_{\text{eff}}$  at the thermal energy ( $\sim 0.025$  eV). All results were found in the interval between 3.5 (no cube) and 4.2 (basis described above). The experimental value is 3.92 (Coleman *et al.* [2]). In Fig. 1 we present our calculated elastic integral cross section for  $e^+$ -He scattering along with some of the available experimental data [8,9] and other theoretical results [10,11]. We see that our cross sections lie below the experimental points [8,9] for energies lower than 2.5 eV and are very close to them for energies between 2.5 and 5 eV. In the limit of zero energy, the experimental cross sections apparently agree better with our results. As seen in this figure our cross sections are a little better than those obtained by McEachran *et al.* [10] using the polarized orbital method, but worse (for energies between 0.5 and 2 eV) than those obtained by Campeanu and Humberston [11] using what they call the H5 model (Kohn variational method). In Fig. 2 we present our static (S) and static-plus-polarization (SP)  $Z_{\text{eff}}$  along with the experimental value of Coleman *et al.* [2] and the theoretical results from Refs. [10] and [11]. When polarization effects are taken into account, our  $Z_{\text{eff}}$ 's are in good agreement (between 5% and 10% difference) with other theoretical

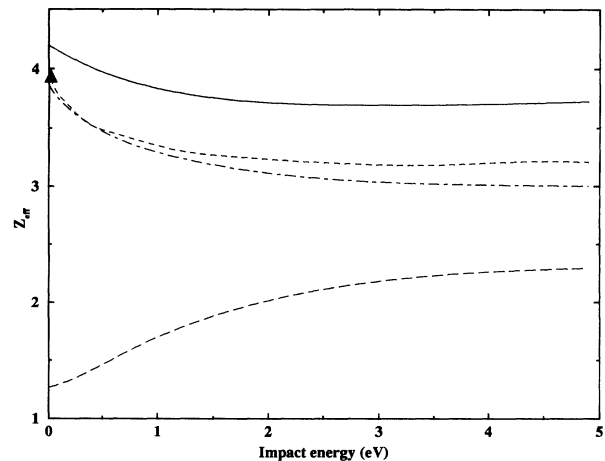


FIG. 2.  $Z_{\text{eff}}$  for  $e^+$ -He scattering. Experimental results: triangle, at thermal energy (0.025 eV) of Coleman *et al.* [2]. Theoretical curves: solid line, present (SP) results; long-dashed line, present (S) results, dot-dashed line, results of McEachran *et al.* [10]; dashed line, results of Campeanu and Humberston [11].

results for all energies. It is clearly seen in this figure that polarization effects are very important in the evaluation of this parameter.

#### IV. RESULTS FOR $\text{H}_2$

We have chosen  $\text{H}_2$  for a first test of Eqs. (10) and (11) for molecules. The SCF wave function for its ground state was obtained with a [7s4p] Cartesian Gaussian basis, at an internuclear separation of  $1.40028a_0$  and has given an electronic energy of  $-1.8473$  hartrees. The exponents are those of Gibson *et al.* [12], except that we added one  $s$  function with exponent 0.035 and we removed two  $p$  functions corresponding to the largest and the smallest exponent of their  $p$  basis. To construct the closed-channel space we used again all possible single-particle excitations to a set of simple virtual orbitals made with the same SCF basis plus additional functions ( $1p_x1p_y$  on a dummy center located at the origin with exponents 0.03, and  $p$  functions at the corners of a cube—same as in He, except that here we have not included the  $s$  functions at the cube faces). We have 64 Gaussian functions for the SMC and we used all symmetries summing up 4096 configurations now. In Fig. 3 we show the elastic integral cross sections for  $e^+$ - $\text{H}_2$  scattering at low energies. We see that our results are in excellent agreement with the experimental data [13,14] for all energies between 1 and 4.9 eV (the presence of the  $p$  functions at the corners of the cube improved substantially our results compared to our previous application [4]). The present results are in good agreement with the Gibson theoretical calculation using the distributed positron model [15] and differ from the  $R$ -matrix results of Danby and Tennyson [16] at lower energies. In Fig. 4 we have our static (S) and static-plus-polarization (SP)  $Z_{\text{eff}}$  along with the experimental value of Heyland *et al.* [3] and the theoretical results of Ar-

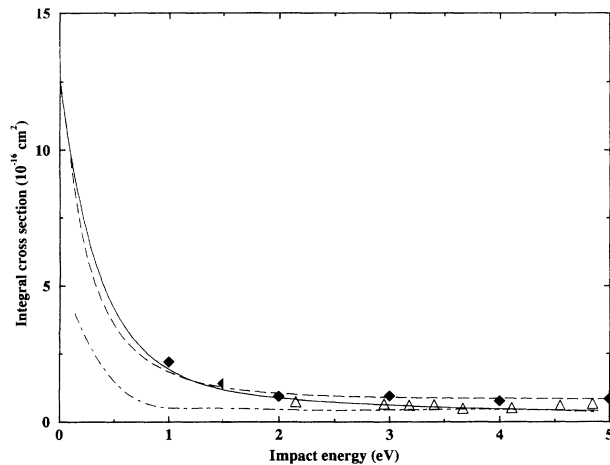


FIG. 3. Elastic integral cross sections for  $e^+$ -H<sub>2</sub> scattering at low energies. Experimental points: diamond, Hoffman *et al.* [13]; triangle, Charlton *et al.* [14]. Theoretical curves: solid, present results (SP); dashed, present results (S); dot-dashed, results of Danby and Tennyson [16]; long-dashed, results of Gibson [15].

mour *et al.* [17] and Hara [18]. Our  $Z_{\text{eff}}$  (SP) is bigger than those of Armour *et al.* [17] and Hara [18] for all energies. Once more, we see the great importance of polarization in the  $Z_{\text{eff}}$  calculation. At the thermal energy, our calculated  $Z_{\text{eff}}$  (13.63) is in excellent agreement with the experimental value (14.7).

## V. CONCLUSIONS

In summary, we have presented fully *ab initio* calculations for the annihilation parameter  $Z_{\text{eff}}$ . We used the total wave function of the Schwinger multichannel method to calculate a electronic property of the system (other than the usual scattering amplitude). Our results look very good when compared to the experimental data

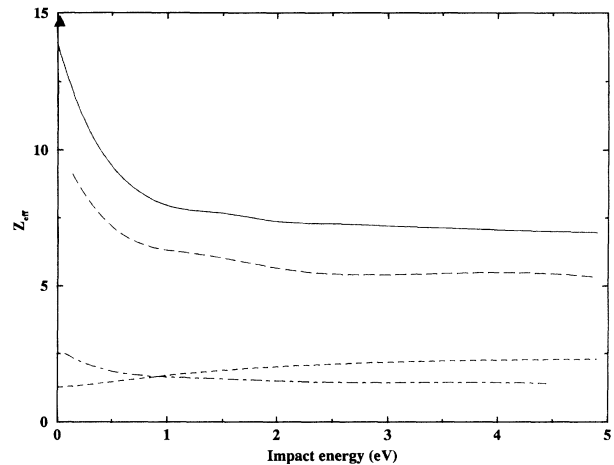


FIG. 4.  $Z_{\text{eff}}$  for  $e^+$ -H<sub>2</sub> scattering at low energies. Experimental points: triangle, Heyland *et al.* [3]. Theoretical curves: solid, present results (SP); dashed, present results (S); long-dashed, results of Armour *et al.* [17]; dot-dashed, results of Hara [18].

at thermal energies. Our next task will be to test our procedures for calculating the parameter  $Z_{\text{eff}}$  for bigger molecules, such as CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>.

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