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Positron impact electronic excitation of N_2

Puspitapallab Chaudhuri, Márcio T. do N. Varella, Claudia R.C. de Carvalho, Marco A.P. Lima *

Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), 13083-970 Campinas, São Paulo, Brazil

Abstract

We present the results of scattering cross sections for positron impact excitation of electronic states of nitrogen molecule (N_2) using the Schwinger multichannel method (SMC). All calculated cross sections took three collision channels into account ($X^1\Sigma_g$ and degenerate $a^1\Pi_g$ states). Present theoretical results for excitation to the $a^1\Pi_g$ states failed to reproduce the near-threshold structure observed in the recent and the only available experimental data [Sullivan et al., Phys. Rev. Lett. 87 (2001) 073201-1]. Scattering calculations from the $a^1\Pi_g$ states (elastic and superelastic) are also reported. A spurious resonant structure found in the excitation to the $a^1\Pi_g$ states was detected in a square integrable basis set calculation designed to reproduce the first Born approximation (FBA). Such spurious structure was removed by taking out the trial configuration state functions in which the positron was weakly coupled to the target. This may be a promising technique to separate unphysical resonances from the physical ones. We also observe that a combination between SMC scattering amplitudes ($l \leqslant 2$) with FBA ones ($l \geqslant 3$) significantly improved the cross sections at higher energies.

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1. Introduction

The development of the high resolution ($\Delta E \sim 25$ meV FWHM) beam of positrons using the highly efficient buffer-gas positron accumulation technique (modified Penning–Malmberg trap) has opened up a new era in the study of positron physics [1–3]. The bright low-energy monochromatic positron beam allows experimentalists to perform highly sophisticated scattering experiments where measurements of state-resolved absolute cross sections for electronic, or vibrational excitations are possible. This experimental breakthrough finds useful applications in several other areas like material science, atomic physics, plasma physics and mass spectroscopy [4]. Moreover, they serve as a strong motivation for the theorists to extend their calculations to investigate in more detail the finer aspects of the scattering process in order to better understand the experimental findings and the underlying physical facts.

Recently, Surko and his collaborators performed a series of highly precise experiments on the electronic excitation of Ar, CO_2, H_2 and N_2 in the energy range from 5 to 30 eV [2]. Motivated by their experiments we have taken up the task to investigate the electronic excitation of N_2

* Corresponding author. Tel.: +55-19-788-5415; fax: +55-19-788-5427.
E-mail address: maplima@ifi.unicamp.br (M.A.P. Lima).

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theoretically. The N_2 molecule is of particular interest as it is very effective as buffer gas. The highly energized positrons lose energy by inelastically colliding against nitrogen molecules thus getting trapped in the accumulator. It is known that out of several possible inelastic processes the electronic excitation is the most effective and participating one in the trapping process [5].

2. Theory

In the present work we have used the Schwinger multichannel method (SMC) for positrons. The SMC, by now, is considered to be a standard many-body approach for theoretical studies on the low-energy scattering of either electrons or positrons by molecular targets. The method has been discussed elaborately in several previous publications [6–8]. Hence, we present no details here, but a few working expressions for the sake of completeness. The scattering amplitude is given by

$$f_{\vec{k}_i\vec{k}_f} = -\frac{1}{2\pi}\sum_{m,n}\langle S_{\vec{k}_f}|V|\chi_m\rangle(d^{-1})_{mn}\langle\chi_n|V|S_{\vec{k}_i}\rangle, \qquad (1)$$

where

$$d_{mn} = \langle\chi_m|A^{(+)}|\chi_n\rangle \qquad (2)$$

and

$$A^{(+)} = Q\hat{H}Q + PVP - VG_P^{(+)}V. \qquad (3)$$

In the above expressions, $S_{\vec{k}_i}$ is a solution of the unperturbed Hamiltonian (molecular Hamiltonian plus the kinetic energy operator for the incident positron); V is the interaction potential between the incident positron and the molecular target; $|\chi_m\rangle$ is a *configuration* state, i.e. an $(N+1)$-particle variational trial function (the product of a target state and a positron scattering orbital). P and Q are, respectively, projection operators onto energetically open and closed electronic states of the target,

$$P = \sum_{l}^{\text{open}}|\Phi_l(\vec{r}_1,\ldots,\vec{r}_N)\rangle\langle\Phi_l(\vec{r}_1,\ldots,\vec{r}_N)|, \qquad (4)$$

with

$$Q = 1 - P. \qquad (5)$$

Finally, $\widehat{H}$ is the collision energy minus the full scattering Hamiltonian and $G_P^{(+)}$ is the free-particle Green's function projected onto P space.

In this work, we consider electronic excitation to the $a^1\Pi_g$ states (from the $X^1\Sigma_g$ state), its reverse superelastic process ($a^1\Pi_g \rightarrow X^1\Sigma_g$) and elastic scattering from the $a^1\Pi_g$ states. The latter involves purely elastic collisions plus zero-energy electronic excitation to degenerate components,

$$\sigma_{\text{elas}}^{\Pi_g} = \frac{1}{2}\left(\sum_{\nu=x,y}\sum_{\mu\neq\nu}\sigma_{\Pi_{g\nu}\rightarrow\Pi_{g\nu}} + \sigma_{\Pi_{g\nu}\rightarrow\Pi_{g\mu}}\right). \qquad (6)$$

Strictly speaking, excitation to degenerate components is not an elastic process in view of the spin–orbit coupling. However, neither fine structure corrections are taken into account in the scattering Hamiltonian nor experimental resolution is able to distinguish the zero-energy electronic excitation from purely elastic scattering.

3. Computational aspects

The Cartesian Gaussian basis set used for both bound state and scattering calculations is given elsewhere [9]. The target ground state was described at the restricted Hartree–Fock (HF) level, while the improved-virtual-orbital (IVO) approximation [10] (out of the $3\sigma_g$ orbital) was used for description of unoccupied orbitals. The nuclei were held fixed throughout the collision (fixed-nuclei approximation).

4. Results and discussions

Excitation to the $a^1\Pi_g$ states was studied with a three-state ($3S$) approximation that included the elastic ($X^1\Sigma_g \rightarrow X^1\Sigma_g$) plus degenerate inelastic ($X^1\Sigma_g \rightarrow a^1\Pi_g$) transitions. Each excited state was obtained by promoting an electron from the $3\sigma_g$ orbital to either π_{gx} or π_{gy} IVOs (single excitations). In such calculation, we noticed a near-threshold structure around 14 eV, which behaved like a core-excited shape resonance associated with the global $^2\Pi_g$ symmetry. This fact is quite relevant because measurements [2] indeed present a

striking near-threshold enhancement in the electronic excitation cross section. Although the authors did not discuss the nature of the observed structure, it would be the first shape resonance reported in low-energy positron scattering [11]. We mention in passing that a shape resonance in positron–copper scattering was considered in a recent theoretical article [12].

However, it must be pointed out that a calculation similar to ours did not present resonant structures at all [13]. Even though our variational Cartesian basis set provided elastic cross sections in very good agreement with experimental data [9], it may not be as suitable for electronic excitation. First, the elastic calculations carefully took polarization effects into account by including a very large number of configurations in the Q (closed-channel) space. As a result, the interaction range was enlarged thus reducing the risk of spurious numerical linear dependency. (It is also true that the inclusion of excited electronic channels is expected to expand the interaction region, but it is not certain how significant such effect would be in a simple $3S$ approximation.) Moreover, estimates of electronic excitation cross sections within the variational SMC framework could be a more delicate matter as compared to elastic processes. The latter have larger cross sections (typically by one order of magnitude) and the related variational coefficients would be favored.

We therefore decided to figure out some criteria to check the quality of variational basis sets and the comparison with the first Born approximation (FBA) turned out to be a suitable approach. Simple as it is, the FBA is attractive in view of its stability (nearly basis-set independent),

$$f_{\vec{k}_i\vec{k}_f}^{\mathrm{FBA}} = -\frac{1}{2\pi}\int \mathrm{d}^3 r\, \mathrm{e}^{\mathrm{i}(\vec{k}_i-\vec{k}_f)\cdot\vec{r}}\langle \Phi_f|V|\Phi_i\rangle. \tag{7}$$

In Eq. (7), V is the positron-target interaction potential while Φ_i and Φ_f are initial and final electronic states of the target, respectively. In order to compare SMC with FBA results, it should be recalled that the latter is valid in the weak interaction limit, $V \to 0$. Hence, by switching off the correlation–polarization effects ($Q\hat{H}Q = 0$) and by neglecting the second order term $VG_P^{(+)}V$, we may rewrite Eqs. (1) and (3) as

$$A^{(+)} \to PVP \Rightarrow f_{\vec{k}_i\vec{k}_f} = -\frac{1}{2\pi}\sum_{m,n}\langle S_{\vec{k}_f}|V|\chi_m\rangle[(PVP)^{-1}]_{mn}\langle\chi_n|V|S_{\vec{k}_i}\rangle. \tag{8}$$

If we now consider the configurations associated with the P space to be complete enough to expand the weak potential,

$$\sum_{l}^{\text{open}}\sum_{m}|\varphi_m\Phi_l\rangle\langle\Phi_l\varphi_m| \simeq 1, \tag{9}$$

where φ_m is a positron scattering orbital, Eq. (1) becomes

$$f_{\vec{k}_i\vec{k}_f} = -\frac{1}{2\pi}\langle S_{\vec{k}_f}|V|S_{\vec{k}_i}\rangle = f_{\vec{k}_i\vec{k}_f}^{\mathrm{FBA}}. \tag{10}$$

Eq. (10) provides a way to represent the FBA in a square-integrable basis set and will be henceforth referred to as the basis-set Born approximation (BSBA).

In the first round of calculations, BSBA results were quite different from those obtained with the FBA. While FBA provided a structureless excitation cross section to the $a^1\Pi_g$ states (Fig. 1, dotted line), BSBA gave rise to a resonant structure and to a much larger cross section magnitude (see the inset of Fig. 1). Such a resonance in the Born approximation is clearly spurious because the

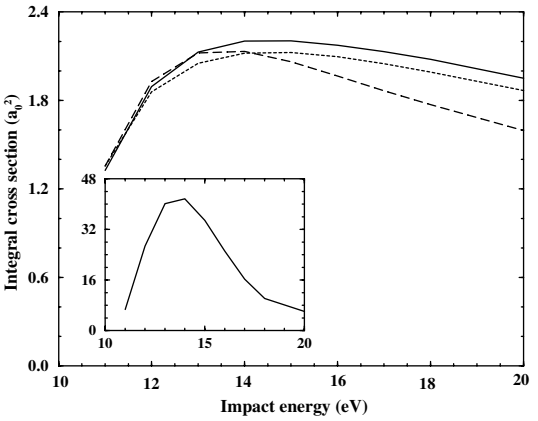

Fig. 1. Integral cross section for the excitation to the $a^1\Pi_g$ states of N_2 by positron impact. Dotted line: FBA result; dashed line: cut-BSBA result; solid line: cut-BSBA + FBA result. The inset shows the BSBA result (all configurations).

weak interaction potential would not be attractive enough to trap the positron. The underlying mechanism leading to the spurious resonance would be as follows. In some configurations associated with diffuse scattering orbitals, the positron would be far from the target, leading to very small potential matrix elements, $V_{mn} = \langle \chi_m | V | \chi_n \rangle$. Since the d_{mn} matrix, given in Eq. (2), must be inverted according to Eq. (1), these nearly zero matrix elements will lead to spurious structures (bumps) in the scattering amplitude. Physical shape resonances would also be associated with nearly singular denominators, but in this case the small matrix elements would be due to a well-accommodated (trapped) positron in the field of the target. Hence, one of the most attractive features of the SMC approach, namely the possibility of well-describing the scattering wave function only in the vicinity of the target ($V \neq 0$) thus allowing approximate $\mathscr{L}^2$ solutions of the scattering problem, also brings the disadvantage of intrinsically short-ranged potentials. If two diffuse Gaussian orbitals happen to remain very close to each other within the interaction region (that is, if they are appreciably distinguishable only at $r \to \infty$) they will give rise to numerical linear dependency. In the SMC scattering amplitude, physical and unphysical resonances (small matrix elements in d_{mn}) would be mixed up, while only spurious structures survive in the BSBA due to the vanishing potential of Eq. (8). In this sense, comparison between FBA and BSBA may provide an efficient means of removing unphysical structures.

In fact, we sorted the potentially troublesome configurations by inspecting the eigenvalues of the V_{mn} matrix. It should be recalled that the SMC framework uses $\mathscr{L}^2$ trial basis sets (products of target states by positron scattering orbitals) thus allowing the (discrete) representation and the diagonalization of $(N+1)$-body operators. Any set of eigenvectors will provide a trial basis set for the scattering amplitude, according to Eq. (1). Once the V_{mn} matrix had been diagonalized, the eigenvectors associated with the lowest eigenvalues (absolute value) were removed in order to improve the agreement between FBA and BSBA. The threshold $|V_{mn}| \geqslant 0.002$ Hartree lead to an agreement better than 1–2% for partial cross sections up to $l = 2$. In this situation, 17 out of 276 configurations (eigenvectors) were taken out. It may be shown that the annihilation parameter (Z_{eff}) provided by the BSBA should be always equal to Z, the number of target electrons. This result was verified within 8–10% at all impact energies after removing the 17 configurations with eigenvalues below threshold. The BSBA result after removing these 17 configurations (cut-BSBA) is also presented in Fig. 1 (dashed line). A very good agreement with FBA is noticed close to the excitation threshold, even though a poor description of the higher partial waves ($l \geqslant 3$) causes the cut-BSBA cross section to become smaller beyond 14 eV. The cut-BSBA was further improved by a closure procedure in which the lowest partial waves ($l \leqslant 2$) of the scattering amplitude are calculated with the cut-BSBA and the higher ones ($l \geqslant 3$) with the FBA. The excitation cross section obtained with the closure procedure (cut-BSBA + FBA) is shown in Fig. 1 (solid line) and a fairly good agreement with the FBA result is observed in the full range of collision energies. For the sake of completeness, we present the related differential cross sections (DCS) obtained with the different Born approximations (FBA, cut-BSBA and cut-BSBA + FBA) in Fig. 2. It is clear that the three approximations provide similar results at higher scattering angles ($\theta > 60°$), although cut-BSBA deviates from the other ones around the forward scattering direction. This was due to the poor description of the potential tail (higher partial waves) and was remedied by the closure procedure.

As mentioned above, the SMC $X^1\Sigma_g \to a^1\Pi_g$ excitation cross section ($3S$ approximation) obtained with all configurations presented a resonant structure associated with the global $^2\Pi_g$ symmetry (see the inset of Fig. 3). We then performed a new SMC calculation with the reduced configuration space (cut-SMC), that is, by removing the 17 configurations with the lowest eigenvalues of the V_{mn} matrix. The result is presented in Fig. 3 (dashed line) and no resonance is noticed at all. Description of higher partial waves was improved through a closure procedure combining the cut-SMC scattering amplitude ($l \leqslant 2$) with the FBA one ($l \geqslant 3$). This final $3S$ calculation (cut-SMC + FBA) for the excitation to $a^1\Pi_g$ states is

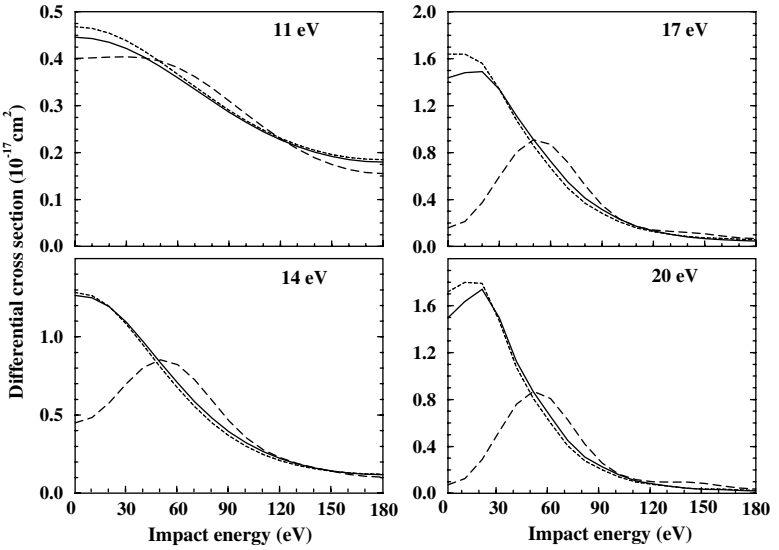

Fig. 2. Differential cross section for the excitation to the $a^1\Pi_g$ states of N_2 by positron impact. Dotted line: FBA result; dashed line: cut-BSBA result; solid line: cut-BSBA + FBA result.

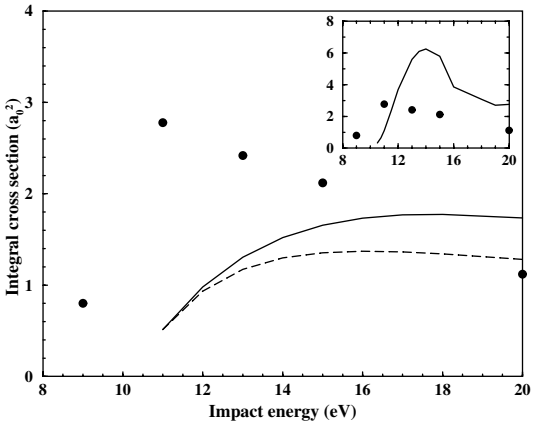

Fig. 3. Integral cross section for the excitation to the $a^1\Pi_g$ states of N_2 by positron impact. Dashed line: cut-SMC result; solid line: cut-SMC + FBA result; bullets: experimental data of [2]. The inset shows the SMC result (all configurations).

also shown in Fig. 3 (solid line). One notices a significant contribution from higher partial waves beyond 12 eV. The related DCS are presented in Fig. 4 and the effect of the closure procedure is once more observed at small scattering angles.

Even though our best result (cut-SMC + FBA) did not reproduce the near-threshold structure observed in the experimental data [2], we cannot come to final conclusions based solely on a simple $3S$ calculation. Three-channel approximations are not expected to be quantitatively accurate because they disregard important dynamical couplings to other collision channels (either open or closed) and the relative positions of excitation thresholds may lead to either core-excited or Feshbach resonances. Moreover, the HF approximation provides a too packed $3\sigma_g$ orbital [14], thus causing the calculated excitation threshold (10.347 eV) to lie almost 2 eV above the experimental value (8.549 eV).

Finally, in Fig. 5 we present cross sections for superelastic scattering from the $a^1\Pi_g$ states (cut-SMC results). Again, we performed three-channel calculations including elastic $a^1\Pi_g \rightarrow a^1\Pi_g$ plus superelastic $a^1\Pi_g \rightarrow X^1\Sigma_g$ collision channels. In general, the magnitude of the elastic cross section is very large. This could be due to a lack of polarization effects which play a crucial role in $X^1\Sigma_g \rightarrow X^1\Sigma_g$ scattering [9]. The elastic $a^1\Pi_g \rightarrow a^1\Pi_g$ cross section also presents an interesting feature, namely a threshold enhancement. However, this behavior should be strongly affected by the improvement of the approximations, that is, by coupling to either open or closed collision channels (polarization effects) or by a better description of excitation thresholds.

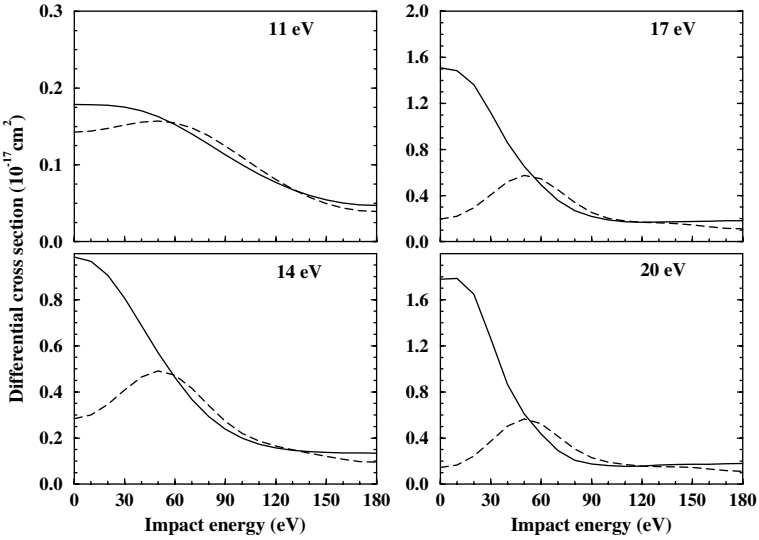

Fig. 4. Differential cross section for the excitation to the $a^1\Pi_g$ states of N_2 by positron impact. Dashed line: cut-SMC result; solid line: cut-SMC + FBA result.

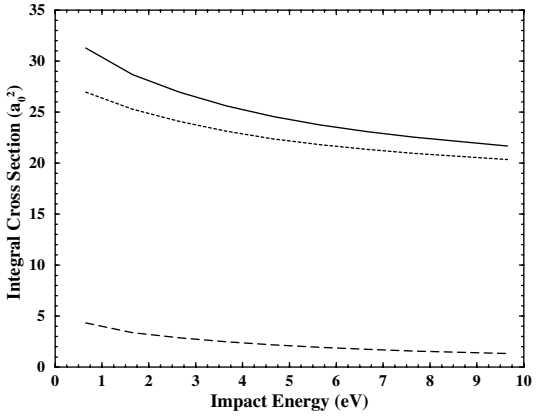

Fig. 5. Integral cross section for superelastic scattering from the $a^1\Pi_g$ states of N_2. Solid line: total cross section (elastic $a^1\Pi_g \rightarrow a^1\Pi_g$ plus superelastic $a^1\Pi_g \rightarrow X^1\Sigma_g$); dotted line: elastic cross section ($a^1\Pi_g \rightarrow a^1\Pi_g$); dashed line: superelastic cross section ($a^1\Pi_g \rightarrow X^1\Sigma_g$).

5. Conclusions

We have presented calculations for the excitation to the $a^1\Pi_g$ states of N_2 molecule by positron impact. Our simple three-channel calculations did not reproduce the near-threshold enhancement observed in the experimental cross section [2]. We have also performed three-channel calculations for positron scattering from the $a^1\Pi_g$ states. A spurious core-excited shape resonance associated with the global $^2\Pi_g$ symmetry could be detected by comparing FBA and BSBA calculations. The spurious structure was related to configurations in which the e^+–N_2 interaction was very weak. Such configurations could be identified by inspection of diagonal elements of the V_{mn} matrix and were then removed. This technique may be a promising procedure to separate unphysical (spurious) resonances from physical ones because the latter are never expected to show up in BSBA calculations (vanishing interaction limit). Finally, we observe that the closure procedure (cut-SMC + FBA) significantly improved the higher partial waves ($l \geqslant 3$) of excitation cross sections.

Acknowledgements

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References

[1] S.J. Gilbert, J.P. Sullivan, R. Greaves, C.M. Surko, Nucl. Instr. and Meth. B 171 (2000) 81.
[2] J.P. Sullivan, J.P. Marler, S.J. Gilbert, S.J. Buckman, C.M. Surko, Phys. Rev. Lett. 87 (2001) 073201-1.
[3] J.P. Sullivan, S.J. Gilbert, C.M. Surko, Phys. Rev. Lett. 86 (2001) 1494.
[4] C.M. Surko, New Directions in Antimatter Chemistry and Physics, Kluwar Academic Publishers, 2001, p. 345.
[5] T.J. Murphy, C.M. Surko, Phys. Rev. A 46 (1992) 5695; R.G. Greaves, M.D. Tinkle, C.M. Surko, Phys. Plasmas 1 (1994) 1439.
[6] J.S.E. Germano, M.A.P. Lima, Phys. Rev. A 47 (1993) 3976.
[7] E.P. da Silva, J.S.E. Germano, M.A.P. Lima, Phys. Rev. A 49 (1994) R1527; E.P. da Silva, J.S.E. Germano, M.A.P. Lima, Phys. Rev. Lett. 77 (1996) 1028.
[8] E.P. da Silva, J.S.E. Germano, J.L.S. Lino, C.R.C. de Carvalho, A.P.P. Natalense, M.A.P. Lima, Nucl. Instr. and Meth. B 143 (1998) 140.
[9] C.R.C. de Carvalho, M.T. do N Varella, E.P. da Silva, J.S.E. Germano, M.A.P. Lima, Nucl. Instr. and Meth. B 171 (2000) 33.
[10] W.J. Hunt, W.A. Goddard III, Chem. Phys. Lett. 24 (1974) 464.
[11] J.P. Sullivan, S.J. Gilbert, S.J. Buckman, C.M. Surko, J. Phys. B 34 (2001) L467.
[12] M.W.J. Bromley, J. Mitroy, Phys. Rev. A 67 (2003) 062709.
[13] T.N. Rescigno, private communication, 2003.
[14] A. Szabo, N.S. Ostlund, Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, McGraw-Hill, New York, 1989.