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A Theoretical Study on e-CO Elastic Collision Using the Configuration Interaction Method to Describe the Target

A Theoretical Study on e⁻-CO Elastic Collision Using the Configuration Interaction Method to Describe the Target

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It is presented a theoretical study on electron -CO collisions in the (5-20) eV energy range. Specifically, elastic differential cross sections (DCS) are calculated using the configuration interaction (CI) method to describe the target. Static and exchange contributions to the interaction potential are obtained exactly from a CI wave function with single and double excitations. The DCS are obtained using the Schwinger variational iterative method (SVIM). It is observed that the discrepancies between Hartree-Fock and CI results are more significant for low energies and small angles.

I. INTRODUCTION

Electron-molecule scattering is a problem of fundamental importance to many areas of pure and applied science, such as radiation physics or modeling of atmosphere and astrophysical systems. In this context it is natural the existence of a strong interest in both experimental and theoretical aspects of this problem. In particular extensive experimental studies in the low energy range ($\varepsilon \leq 50$ eV) have been performed on a wide variety of systems from small to more complex molecules. An example of such a system is the CO molecule. It plays an important role in physical and chemical processes such as laser, gas discharges and plasmas [1]. In addition this molecule is a constituent of our own atmosphere and of the interstellar medium.

Several experimental studies on e⁻-CO interaction have been presented in the literature over the past decades. For instance, rotational excitations cross sections were studied by Sohn *et al*. [2] and Gote and Ehrhardt [3], and vibrational excitation processes by Chutjian and Tanaka [4], Tronc *et al*. [5] and Gibson *et al*. [6]. Cross sections for elastic, vibrational excitations and electronic excitations leading to some lying states of CO were reported by Middleton *et al*. [7]; elastic differential cross sections (DCS) measurements have also been performed by Nickel *et al.* [8] and elastic and vibrational cross sections by Jung *et al.* [9]. In addition a substantial number of measurements of the total (elastic + inelastic) cross sections has been presented in the literature [10–12].

From the theoretical viewpoint several methods have been used in the study of low-energy electron scattering by molecules (for a review see for example [13]) including multiple scattering models, the R-matrix method and the Schwinger variational method, among others. For e⁻-CO collisions, however, comparatively to experimental results there are much less theoretical investigations. Specifically, some earlier studies were carried out at the static-exchange (SE) level of approximation [14, 15]; Jain and Norcross have used an exact SE plus parameter-free polarization model (SEP) to deter-

mine rotationally elastic and inelastic DCS and integral cross sections [16] for incident energies up to 10eV. The R-matrix approach has been used by Morgan [17], Morgan and Tennyson [18], Salvini *et al.* [19] and also by Gibson *et al.* [6] in order to determine cross sections for both elastic and vibrational excitation. A combination of the Schwinger variational iterative method (SVIM) and the distorted-wave approximation (DWA) has been used by Lee *et al.* [20] in the low and intermediate energy ranges.

In the framework of single channel calculations based on SVIM, the static and exchange potentials are usually determined by using a Hartree-Fock (HF) function to describe the target. In consequence, electronic correlation effects in the target are not included in these theoretical results. This fact has consequences for low energy process; for example, elastic DCS present, in some cases, quantitative and/or qualitative discrepancies when compared to the measured data [21]. In fact, it is known from modern atomic and molecular electronic structure theory that the Hartree Fock approximation, while remarkably successful in most cases, has some limitations and problems [22–25]. In particular, in more recent molecular calculations the HF approximation is frequently used as a starting point for more accurate approximations such as the configuration interaction (CI) method, the multireference CI (MRCI) and the many-body perturbation theory (MBPT), that include correlation effects [25, 26].

In the present communication we perform a calculation of elastic e⁻-CO DCS using the CI method to describe the target, thus determining both static and exchange potentials. We will denote this approach by CI-SE model. From our results it is possible to analyse how the target electronic correlation (static correlation) influences the elastic DCS at the SE level. We point out the importance of these calculations for the low energy range by comparing our method to the conventional (Hartree-Fock) SVIM in the level SE. In our calculations we will not consider dynamical correlation (polarization effects). In fact, our objective here is to show the importance of target correlation for a reliable description of elastic e⁻-CO. Hence

we have considered energies above the resonance region in order to avoid the superposition of both dynamical and static correlation effects since for higher collision energies the dynamical correlation is known to be less important.

The organization of the paper is as follows. In section II we present some theoretical details on the Schwinger variational iterative method (SVIM) and the CI-SE model. In section III we present some details of the calculations. In section IV we compare our calculated results with experimental data and other theoretical results reported in the literature. Finally, in section V, we summarize our conclusions.

II. THEORY

Since the details of the SVIM and the CI method applied to scattering theory have already been presented in previous works [27, 28] only a brief outline of the theory will be given here.

The electron-molecule collision is described by Lippmann-Schwinger equation

$$|\Theta\rangle = |\theta\rangle + G_0^\pm U |\Theta\rangle \qquad (1)$$

where $|\Theta\rangle$ is the state function of the interacting electron-molecule system, $|\theta\rangle$ is the corresponding state function without interaction, $G_0^\pm = \lim_{\varepsilon \to 0} (\nabla^2 + k_0^2 \pm i\varepsilon)^{-1}$ is the free-particle Green´s operator and $U = 2V$ is the reduced potential operator. The superscript $+(-)$ denotes the outgoing (incoming) traveling-wave boundary conditions of the scattering function.

In the single-channel scattering theory and coordinate representation, we have

$$\Theta(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; \vec{r}) = \hat{A} \left(\Phi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)\xi(\vec{r}) \right)$$

which satisfies the Schrödinger equation $(\hat{H}_T - E)\Theta(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; \vec{r}) = 0$, that is

$$\left(\hat{H} - \frac{1}{2}\nabla^2 + \sum_A V(|\vec{r} - \vec{r}_A|) + \sum_j V(|\vec{r} - \vec{r}_j|) - E \right)$$
$$\times \Theta(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; \vec{r}) = 0 \qquad (2)$$

where $\hat{A}$ is an antisimetrizer operator, $V(|\vec{r} - \vec{r}_A|)$ is the potential interaction between the scattering electron and the nucleus at $\vec{r}_A$, $V(|\vec{r} - \vec{r}_j|)$ is the interaction potential between the j-th electron and the scattering electron; $-\frac{1}{2}\nabla^2$ refers to the kinetic operator of the scattering electron and $\hat{H}$, the N-electron molecule Hamiltonian, is given by

$$\hat{H} = \sum_i^N h(i) + \sum_{j<\ell}^N \frac{1}{r_{j\ell}} \qquad (3)$$

In equation (3) $h(i)$ is the Hamiltonian operator for the i-th electron moving in the potential of the nuclei A, B, ... alone and $r_{j\ell}$ is the distance between the j-th and ℓ-th electron. For $\hat{H}$ we have

$$\hat{H}|\Phi_0\rangle = \mathcal{E}_0|\Phi_0\rangle \qquad (4)$$

and by projecting equation (2) on $\Phi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$, we obtain

$$\left(\nabla^2 + k_0^2 \right) \xi(\vec{r}) = U_0 \xi(\vec{r}) \qquad (5)$$

where the kinetic energy of the incident electron satisfies the relation $\frac{1}{2}k_0^2 = E - \mathcal{E}_0$. In this work we have used the Schwinger variational iterative method (SVIM) [27] for the calculation of $\xi(\vec{r})$ and the interaction potential U_0 is determined from a target CI (configuration interaction) wavefunction $\Phi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$.

In SVIM calculation, the continuum wavefunctions are single-center expanded as

$$\xi_{\vec{k}}^{(\pm)}(\vec{r}) = \left(\frac{2}{\pi} \right)^{1/2} \frac{1}{k} \sum_{lm} i^\ell \xi_{klm}^{(\pm)}(\vec{r}) Y_{lm}^*(\hat{k}). \qquad (6)$$

In pratice the summation in l, m is truncated to some cutoff values l_c, m_c. To proceed, a set of $\mathcal{L}^2$ functions is used to represent the initial trial scattering wavefunction. In our work, a set of Cartesian Gaussian basis functions R_0 is chosen for this purpose. Improvement of the scattering wavefunctions is achieved via an iterative procedure that consists basically of augmenting the basis set R_0 by the set S of the partial-wave components $\xi_{klm}^{(\pm)}(\vec{r})$. The new augmented set, $R_1 = R_0 \cup S$ is used as a new basis for obtaining a new set S' of improved wavefunctions $\xi_{\vec{k}}^{(\pm)}(\vec{r})$. In the sequence $R_2 = R_0 \cup S'$ is now used as a new basis set and a set S'' is determined. Hence we consider $R_3 = R_0 \cup S''$ and this procedure is continued until converged $\xi_{klm}^{(\pm)}(\vec{r})$ are obtained [27]. These converged scattering wavefunctions correspond, in fact, to exact solutions of the truncated Lippmann-Schwinger equation with SE potential.

The configuration interaction (CI) many-electron function $|\Phi_0\rangle$ is written, in usual notation, as

$$|\Phi_0\rangle = C_0|\psi_0\rangle + \sum_{a,r} C_a^r|\psi_a^r\rangle + \sum_{a<b r<s} C_{ab}^{rs}|\psi_{ab}^{rs}\rangle + \ldots \qquad (7)$$

where $|\psi_0\rangle$ is a Slater determinant obtained from a self-consistent-field (SCF) Hartree-Fock calculation [29]. The Slater determinant $|\psi_0\rangle = |\chi_1\chi_2 \ldots \chi_a \ldots \chi_b \ldots \chi_N\rangle$ is taken as reference function with $\chi_i = \varphi_i\eta_i$ a molecular spin-orbital (MSO), $\chi_{2i-1} = \varphi_i\alpha_i$, $\chi_{2i} = \varphi_i\beta_i$, $i = 1, 2, \ldots, n$; $\alpha, \beta =$ spin functions and $\varphi_i =$ molecular spatial orbitals. The other determinants $|\psi_{ab\ldots}^{rs\ldots}\rangle$ are obtained from $|\psi_0\rangle$ by considering excitations from the occupied MSOs $\chi_a, \chi_b, \ldots$ to virtual MSOs $\chi_r, \chi_s, \ldots$. The coefficients C_a^r, C_{ab}^{rs}, ... are determined by diagonalizing the target Hamiltonian $\hat{H}$ given in equation (3). Specifically, in the case where we have a finite basis set of $2K \geq N$ MSOs we can construct $M = \binom{2K}{N}$ different N−electron Slater determinants and use these determinants as a basis set to expand the exact many-electron function $|\Phi_0\rangle$.

In the present study the e^--molecule potential scattering is obtained by using $|\Phi_0\rangle$ given by equation (7). Explicity, we have $U_{CI} = 2V_{CI}^S + 2V_{CI}^E$ where

$$V_{CI}^S \xi(\vec{r}) = \sum_{i,j} f(i,j)\langle\chi_i| \frac{1}{|\vec{r}\prime - \vec{r}|} |\chi_j\rangle \xi(\vec{r}) \qquad (8)$$

and

$$V_{CI}^E \xi(\vec{r}) = \sum_{i,j} g(i,j) \langle \chi_i | \frac{1}{|\vec{r}\prime - \vec{r}|} | \xi \rangle \varphi_j(\vec{r}) \eta_j \qquad (9)$$

In equations (8) and (9) a numerical integration with respect to the $\vec{r}\prime$ coordinates is performed and the numerical factors $f(i,j)$ and $g(i,j)$ result dependent on the CI coefficients $C_0, C_{a'}^{s'}, C_{a'b'}^{s't'}, \ldots, C_0^*, C_a^{s*}, C_{ab}^{st*}, \ldots$; they are, therefore, responsible by the inclusion of the electronic correlation in the determination of the interaction potential U_0. We have implemented a set of computational programs to evaluate all factors $f(i,j)$ and $g(i,j)$. They are calculated after the CI equations have been solved.

III. CALCULATIONS

In this study the SE potential has been calculated from a CI many-electron function. We have also used a HF target solution, for comparison. Double Zeta basis sets were used in both the HF and CI calculations, performed using the standard quantum chemistry code GAMESS [30]. The numerical factors $f(i,j)$ and $g(i,j)$ were determined by our computer codes. We have limited the partial-wave expansions of the continuum wavefunction as well as of the T-matrix elements up to $\ell_{max} = 12$. Our results shown below were all converged within five iterations. The normalization of all bound orbitals were better than 0.9998. The basis set R_0 used for the calculation of the initial trial scattering functions is shown in Table1.

TABLE I: Basis set for the calculation of initial trial scattering functions

Symmetry	Basis functions	Exponents
σ	s	8.0, 4.0, 2.0, 1.0, 0.5, 0.2
	z	4.0, 2.0, 1.0, 0.3
π	x	8.0, 4.0, 2.0, 1.0, 0.5, 0.2
	xz	4.0, 2.0, 1.0, 0.3
δ and higher	xy	8.0, 4.0, 2.0, 1.0, 0.5, 0.2

The CO molecule is linear and the experimental equilibrium length is 2.132 au. Our target-correlated CI calculation was performed at the SDCI (CI calculation with single and double excitations) level. The resulting SDCI wavefunction was composed by 969 CSF (configuration state function) with 3784 determinants. The energy of the SDCI wavefunction resulted -112.873 au, to be compared with our Hartree-Fock energy of -112.684 au and with the Hartree-Fock limit of -112.789 au [31]. The corresponding DCS were noted by HF results and SDCI results.

IV. RESULTS AND ANALYSIS

In figures (1- 5) we compare our calculated DCS using CI-SE model for elastic e^--CO scattering with some available

experimental data [6, 8, 32] and DCS obtained from the usual HF calculations [6, 16, 33]. An analysis of these results shows that in the $(5 - 20)$ eV energy range all the calculated DCS in the CI-SE model agree better with the experimental results, both in shape and magnitude, than those obtained from the usual HF wavefunctions. Particularly for energies below 15 eV the good agreement between our calculated CI-DCS and the available experimental values is very meaningful since in this energy range correlation effects are expected to be important. This confirms the validity of our description of elastic collision via the use the CI-method to describe the target and to calculate the interaction potential. In particular for energy $\varepsilon = 15$ eV the comparison of our DCS with existing experimental values shows an excellent agreement, both qualitatively and quantitatively. For energies $\varepsilon \geq 15$ eV we note that the differences between CI-DCS and HF-DCS are less pronounced, thus confirming that the electronic correlation is more important at lower energies. In fact for $5 \leq \varepsilon \leq 15$ eV the DCS obtained using the usual HF are overestimated at small ($\theta < 60^o$) scattering angles, underestimated for $\theta > 130^o$ and in very strong disagreement when compared to the available experimental data. Our CI-DCS results, however, are in very good agreement with these experimental values.
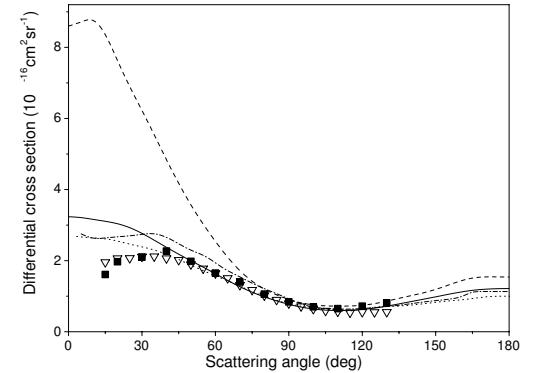

FIG. 1: DCS for elastic electron scattering from CO at energy of 5.0eV. ——, present SDCI results;— — — , present HF results; ······, theoretical results of Gibson *et al.* [6]; — · —, theoretical results of Jain and Norcross [16]; $\triangledown$, experimental data of Gibson *et al.* [6] and ■, experimental data of Tanaka *et al.* [32].

V. CONCLUSIONS

We have presented a study of elastic e^--CO collisions at the SE level using the CI method to describe the target. In consequence this CI-SE model includes target electronic correlation effects (static-correlation). Our CI results were obtained with single (S) and double (D) excitations and the corresponding DCS were compared to the available experimental values and to the usual HF results. Meyer et al [34, 35] in their study of N_2-resonance shape found that it is necessary a multireference CI (MRCI) calculation to obtain a reliable description of the
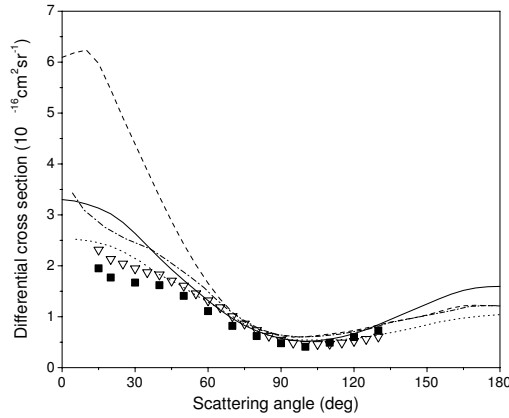
FIG. 2: DCS for elastic electron scattering CO at energy of 7.5eV: ——, present SDCI results; — — —, present HF results; ······, theoretical results of Gibson *et al.* [6]; — · —, theoretical results of Jain and Norcross [16] ; $\bigtriangledown$, experimental data of Gibson *et al.* [6] and ■, experimental data of Tanaka *et al.* [32].
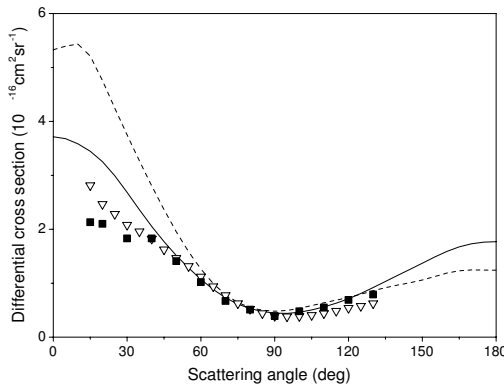

FIG. 4: DCS for elastic electron scattering CO at energy of 15eV: ——, present SDCI results; — — —, present HF results; — · —, theoretical results of Rolles *et al.* [33] and ■, experimental data of Tanaka *et al.* [32].

FIG. 3: DCS for elastic electron scattering CO at energy of 10eV: ——, present SDCI results; — — —, present HF results; $\bigtriangledown$, experimental data of Gibson *et al.* [6] and ■, experimental data of Tanaka *et al.* [32].

FIG. 5: DCS for elastic electron scattering CO at energy of 20eV: ——, present SDCI results; — — —, present HF results; $\bigtriangledown$, experimental data of Gibson *et al.* [6] and ●, experimental data of Nickel *et al.* [8].

potential in the (2-5) eV energy range. Here we have studied elastic e⁻-CO collisions and considered energies above the resonance region in order to avoid the superposition of both dynamic and static correlation effects since for higher collision energies dynamical correlation becomes less important. In fact the main goal of our work is to show the importance of static (isolated target) correlation and this could be hardly done at the resonance energy. On the contrary, the role played by the static polarization is clearly seen at slightly higher energies.

Our results for the elastic e⁻-CO scattering in the (5-20) eV energy range using a SE-potential obtained from CI wavefunctions show that, at these energies: (i) for a given atomic
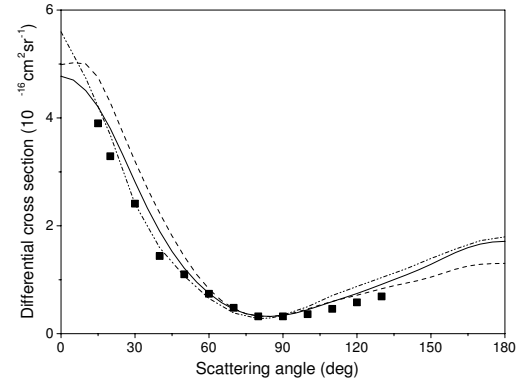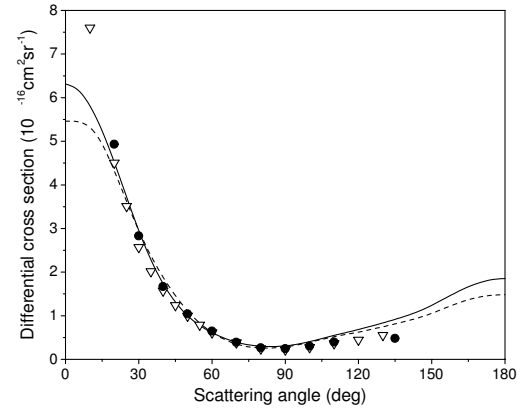
basis set (DZV in our case) higher-than-double excitations are not needed to be included in the CI expansion, since a conventional SDCI calculation is capable of providing theoretical results of DCS in good agreement with experimental values; (ii) in the entire energy range studied here, the CI-DCS are always in better agreement with the available experimental values when compared to the usual HF results at the SE level; (iii) for energies ε ≥ 15 eV the difference between CI-DCS and HF-DCS are less pronounced i.e. the target electronic (static) correlation effects are more important for lower energies. A study of elastic e⁻-CO scattering in resonance energy range, aiming to determine the static, exchange and polarization contributions and to analyze their influence on the DCS using our CI-model, is now in process and will be presented

in near future.

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[1] J. Hahn and C. Junge, Z. Naturf. **32a**, 190 (1977).

[2] W. Sohn, K.-H. Kochem, H. Ehrhardt, and E. S. Chang, J. Phys. B: Mol. Opt. Phys. **18**, 2049 (1985).

[3] M. Gote and H. Ehrhardt, J. Phys. B: Mol. Opt. Phys. **28**, 3957 (1995).

[4] A. Chutjian and H. Tanaka, J. Phys. B: Mol. Opt. Phys. **13**, 1901 (1980).

[5] M. Tronc, R. Azria, and Y. Le Coat, J. Phys. B: Mol. Opt. Phys. **13**, 2327 (1980).

[6] J. C. Gibson, l. A. Morgan, R. J. Gulley, M. J. Brunger, C. T. Bundschu, and S. J. Buckman, J. Phys. B: Mol. Opt. Phys. **29**, 3197 (1996).

[7] A. G. Middleton, M. J. Brunger, and P. J. O. Teubner, J. Phys. B: Mol. Opt. Phys. **25**, 3541 (1992).

[8] J. C. Nickel, C. Mott, I. Nanik, and D. C. McCollum, J. Phys. B: Mol. Opt. Phys. **21**, 1867 (1988).

[9] K. Jung, T. Antoni, R. Muller, K.-H. Kochem, and H. Ehrhardt, J. Phys. B: Mol. Opt. Phys. **15**, 3535 (1982).

[10] C. Szmytkowski, K. Maciag, and G. Karwasz, Physica Scripta **54**, 271 (1996).

[11] G. Karwasz, R. S. Brusa, A. Gasparoli and A. Zecca, Chem. Phys. Lett. **211**, 529 (1993).

[12] O. Sueoka and S. Mori, J. Phys. Soc. Jpn. **53**, 2491 (1984).

[13] F. A. Gianturco, in *The Physics of Electronic and Atomic Collisions* - p. 201 - L. J. Dubé, J. B. A. Mitchell, J. W. Mcconkey, C. E. Brion (Eds.), AIP Press, Woodbury (1995).

[14] D. A. Levin, A. W. Flifet, and V. McKoy, Phys. Rev. A **21**, 1202 (1980).

[15] L. A. Collins, W. D. Robb, and M. A. Morrison, Phys. Rev. A **21**, 488 (1980).

[16] A. Jain and D. W. Norcross, Phys. Rev. A **45**, 1644 (1992).

[17] L. A. Morgan, J. Phys. B: Mol. Opt. Phys. **24**, 4649 (1991).

[18] L. A. Morgan and J. Tennyson, J. Phys. B: Mol. Opt. Phys. **26**, 2429 (1993).

[19] S. Salvini, P. G. Burke, and C. J. Noble, J. Phys. B: Mol. Opt. Phys. **17**, 2549 (1984).

[20] M.-T Lee, I. Iga, L. M. Brescansin, L. E. Machado, and F. B. C. Machado, J. Mol. Structure (Teochem) **525**, 181 (2002).

[21] B. K. Sarpal, K. Pfingist, B. M. Nestmann, and S. D. Peyerimhoff, J. Phys. B: Mol. Opt. Phys. **28**, 857 (1996).

[22] P. E. Cade, K. D. Sales, and A. C. Wahl, J. Chem. Phys. **44**, 1973 (1966).

[23] I. Shavitt *Modern Theoretical Chemistry 3,* edited by H.F.Schaefer III (Plenum, N.Y. 1977).

[24] A. C. Wahl and G. Das, *Methods of Electronic Structure Theory* (New York: Plenum Press, 1977) p.51.

[25] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (New York: Dover Publications Inc., 1996).

[26] J. D. M. Vianna, A. Fazzio and S. Canuto, *Teoria Quântica de Moléculas e Sólidos* (São Paulo: Editora Livraria da Física, 2004).

[27] R. R. Lucchese , G. Raseev, and V. McKoy, Phys. Rev. A **25**, 2572 (1982).

[28] J. D. M.Vianna, M. G. R.Martins, A. M.Maniero, E. M. S. Ribeiro, and L. E. Machado, J. Phys. B: At. Mol. Opt. Phys. **34**, L617 (2001).

[29] C. C. J. Roothaan Rev. Mod. Phys. **23**, 69 (1951).

[30] M. N. Scmidt, K. K. Baldrigek, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jense, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).

[31] P. C. Hariharam and J. A. Pople Theoret. Chim. Acta **28**, 213 (1973).

[32] H. Tanaka, S. K. Srivastava, and A. Chutjian, J. Chem. Phys. **69**, 5329 (1978).

[33] D. Rolles, R. D. Muiño, F. J. Garcia de Abajo, C. S. Fadley, and M. A. Van Hove, Journal of Electron Spectroscopy **114**, 107 (2001).

[34] H.-D. Meyer, S. Pal, and U.V. Riss, Phys. Rev. A *46*, 186 (1992).

[35] H.-D. Meyer, Phys. Rev. A **40**, 5605 (1989).