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Original Investigation

Outer Shell Ionization Potentials for Ethane by a Many-Body Green's Function Method

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A calculation based upon the many-body Green's function method is employed to obtain the outer shell vertical ionization potentials of the ethane molecule. An extended basis set is employed to represent the approximate optical potential, derived by the functional derivative approach, as well as the one-electron Green's function. The results obtained confirm a ^2E_g state for the ion arising from the first ionization process.

Key words: C_2H_6 molecule, ionization potentials of ~ – Many-body Green's function method.

1. Introduction

The ethane molecule has been the subject of several theoretical [1–6] and experimental [7–12] investigations in order to resolve the controversy over the identification of the final state corresponding to the first ionization process. Since the many-body Green's function method has shown to be capable to predict, with good accuracy, the ionization potentials of a wide variety of molecules [13], we have applied it to the ethane molecule.

Here, as in our previous work [14–17], the one-electron Green's function is obtained by solving the Dyson equation projected in a finite basis set. The approximated optical potential employed, derivable from the expression which

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contains its functional derivative with respect to an external potential [18, 19], is analogous to that used previously [14–17]. In this work however, due to the large dimension of the problem, the optical potential was obtained by introducing some further simplifications as described in Sect. 2.

2. Theory

The one-particle Green's function G is obtained by solving directly the Dyson equation [18] with an optical potential approximated by

$$\Sigma(1,6)=\Sigma^{\mathrm{I}}(1,6)+\Sigma^{\mathrm{C}}(1,6) \tag{1}$$

$$\Sigma^{\mathrm{I}}(1,6)=-i\delta(1-6)\int \mathrm{d}2\,V(1-2)G_{\mathrm{HF}}(2,2^{+})+iV(1-6)G_{\mathrm{HF}}(1,6^{+}) \tag{1a}$$

$$\begin{aligned}\Sigma^{\mathrm{C}}(1,6)&=i\int d2d3\,V(1-2)\,V(3-6)R^{\mathrm{RPA}}(323^{+}2^{+})G_{\mathrm{HF}}(1,6)\\&\quad-i\int d2d3\,V(1-2)\,V(3-6)R^{\mathrm{RPA}}(326^{+}2^{+})G_{\mathrm{HF}}(1,3)\end{aligned} \tag{1b}$$

where G_{HF} is the Hartree–Fock independent particle Green's function and R^{RPA} is the Random Phase Approximation to the linear response function [20].

The optical potential Σ^{C} in the energy representation may be formally expressed, employing a finite and real basis set of spin orbitals, as [15]

$$\Sigma^{\mathrm{C}}(\omega)=\sum_{j}\frac{\mathbf{L}_{\bullet j}\tilde{\mathbf{L}}_{\bullet j}}{\omega-d_j}. \tag{2}$$

Since we are interested in the ionization potentials, the Eq. (1b) has been computed exactly only for the terms with $d_j<0$ while the other contributions, deriving from the time ordering $t_6>t_1$ were computed by the second order approximation

$$\begin{aligned}\Sigma^{\mathrm{C}}(1,6)&=i\int d2d3\,V(1-2)\,V(3-6)G_{\mathrm{HF}}(3,2^{+})G_{\mathrm{HF}}(2,3^{+})G_{\mathrm{HF}}(1,6)\\&\quad-i\int d2d3\,V(1-2)\,V(3-6)G_{\mathrm{HF}}(3,2^{+})\\&\quad\times G_{\mathrm{HF}}(2,6^{+})G_{\mathrm{HF}}(1,3)\qquad(t_6>t_1)\end{aligned} \tag{3}$$

This procedure is justified by noticing that the terms of Σ^{C} with negative poles are much more important than the other ones in determining the negative poles and corresponding residues of the resulting G. Thus we expect that the contributions to Σ^{C} from the third order onward (for $t_6>t_1$) may be neglected without perceivable effect on the resulting ionization potentials.

The approximate Dyson equation is solved numerically by the direct diagonalization (DD) method described elsewhere [15].

3. Results and Discussion

The ethane molecule is considered in its staggered equilibrium form (D_{5d} symmetry) with geometrical parameters $R_{CC} = 1.538$ Å, $R_{CH} = 1.086$ Å, $<HCC = 110.7°$. The basis set (of 58 contracted Gaussian functions) consists of six *s* and four *p* functions on each carbon atom and two *s* functions on each hydrogen atom. Four *s* and two swollen *p* functions, located at the inversion center, are added for a better description of the low-lying excited states of the molecule.

An SCF procedure has been carried out for the determination of G_{HF}, obtaining a total energy of -79.21109 a.u.

Table 1 reports the singlet-singlet excitation energies and the corresponding oscillator strengths, as obtained by the RPA calculation. The lowest vertical frequencies of ungerade symmetry are about 2 eV too large in comparison with the experimental data [21–25]. This type of discrepancy, common for the RPA results, is accentuated, in our opinion, by the lack of more diffuse functions in the basis set. It must be emphasized however that, the overall behaviour of the response function may be considered satisfactory.

In fact the sum of the oscillator strengths, which may be taken as an index of the quality of the total response function, is equal to 17.939, in comparison with the exact value 18.

Table 2 reports the Green's function results for the ionization potentials up to 40 eV. The poles λ_j and the corresponding traces of the residues g^j, (only those greater than 0.01) are reported in column 3 and 4 respectively, while the symmetry labels are listed in the first column. The approximations to the ionization potentials given by the Koopman's theorem (ε_{SCF}) are listed in column 2 while the last two columns report the experimental values obtained by photoelectron (PE) and (*e*, 2*e*) spectroscopy.

Differently from the previous investigated systems [15, 16, 17], the trace of the residue matrices has a noticeable value only for few principal poles. Some satellites are found however at an energy greater than 25 eV with a crowding (total trace $\simeq 0.1$) between 29 and 34 eV. The (*e*, 2*e*) spectra [12] show a

Table 1. Lower RPA singlet-singlet excitation energies and dipole oscillator strengths

Symm.	ω_l (eV)	f_l [a]
E_g	9.98	0.0
A_{1g}	10.62	0.0
E_u	11.45	0.311
E_g	11.81	0.0
A_{2u}	11.93	0.287
E_u	12.13	0.047
A_{1u}	12.22	0.058
A_{1g}	12.32	0.0
A_{2u}	12.43	0.131
E_u	12.46	0.143

[a] $f_l = \frac{4}{3}\omega_l |\mathrm{tr}\, X_0^l \mathbf{r}|^2$; see Ref. [15].

Table 2. Results of SCF and Green's function methods and experimental data for outer shell ionization potentials of ethane (eV)

				EXP	
Symm.	$-\varepsilon_{\mathrm{SCF}}$	λ_j	tr g^j	PE	$(e, 2e)$[a]
E_g	13.24	12.32	0.9290	12.0[b] 12.72[b]	12.25
A_{1g}	13.73	12.74	0.9103	13.5[b]	13.35
E_u	16.26	14.94	0.9100	15.35[c]	15.45
A_{2u}	23.04	20.60	0.8389	20.42[c]	21.0
A_{1g}		23.38	0.0339		
A_{1g}	27.72	24.24	0.7753	23.91[c]	24.5
A_{1g}		25.13	0.0143		
A_{1g}		26.34	0.0170		
A_{1g}		29.21	0.0108		
A_{1g}		30.15	0.0179		
A_{2u}		30.54	0.0195		
A_{2u}		31.08	0.0145		
A_{2u}		32.27	0.0100		
A_{1g}		33.59	0.0327		
A_{1g}		37.16	0.0135		
A_{2u}		39.35	0.0110		

[a] Vertical ionization potential from Ref. [12].
[b] By HeI spectroscopy, from Ref. [10].
[c] Vertical ionization potential by ESCA, from Ref. [11].

considerable structure in the range 29–50 eV although the resolution is too poor for a clear identification of the single peaks.

In the 14.5–25 eV region three principal ionization potentials, corresponding to E_u, A_{2u}, and A_{1g} symmetries for the cation electronic state, are obtained by our calculations. The first one is about one half eV lower than the experimental value, while the other two are in good agreement with the results of the ESCA and $(e, 2e)$ spectroscopies.

In the 11.5–14.0 eV range of the experimental spectra, a large band, which displays a noticeable vibronic structure, is found. Two ionization processes, leaving the cation in electronic states ${}^2E_g$ and ${}^2A_{1g}$, are considered responsible of this broad band. A further complication arises from the presence of the Jahn–Teller interaction which splits the E_g band in two peaks so that, in the He I spectrum [10], three maxima are recognized at 12, 12.72 and 13.5 eV. However for a comparison with our calculation of the vertical ionization potentials which neglect the Jahn–Teller effect, the results of high-energy spectroscopies may be considered more suitable. While the available ESCA spectra [7, 11] don't help to clarify the situation in this region, the $(e, 2e)$ spectra [12] reveal a strong overlapping of two bands, whose maxima are localized at 12.25 and 13.35 eV. These maxima, identified by the angular dependence of non coplanar symmetric $(e, 2e)$ reaction are assigned to the formation of ${}^2E_g$ and ${}^2A_{1g}$ cation electronic states respectively. Our results confirm this experimental assignment which is also in agreement with some recent theoretical works [1, 4, 5] although other authors have obtained the opposite order [2, 3, 6].

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